University of California, Irvine

Chemometric Modeling of Select Lanthanides in Solution via Partial Least Squares Regression for Material Accountancy and Safeguarding

Dissertation

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by

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Curriculum Vitae

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Abstract of Dissertation

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By

Edward Kyle Jenner

Doctor of Philosophy in Chemical and Biochemical Engineering

University of California, Irvine, 2019

Professor Mikael Nilsson, Chair

Utilizing nuclear energy to combat climate change is rapidly becoming necessary to mitigate major disruptive events. However, nuclear technology has an inherent dual use concern which creates a challenge to the legitimacy of some nuclear energy programs. Ergo, nuclear energy must be expanded with care of region and country-specific threats to maintain long-term prosperity. One such avenue is implementing spectroscopic on-line monitoring for tracking special nuclear material in close to real time. Using UV/Visible spectrum absorbance implements a barrier to nefarious tampering of a recycling system by utilizing physical properties unique from existing safeguards. In this thesis, optimization of a partial least squares regression model built on UV/Vis absorbance was explored, along with probing of a power analysis to better understand modeling parameters, and the speciation of neodymium with citrate as may be found in advanced nuclear fuel recycling. The models were optimized to maximize accuracy while minimizing susceptibility to deception. Ultimately, an accurate on-line model for special nuclear material will make nuclear recycling a more globally achievable goal, ergo increasing the prevalence of nuclear energy and contributing to climate change abatement.

Chapter 1: Scope of this Thesis

Contained in this thesis is the work I conducted to investigate modeling techniques for optimal material safeguarding in used nuclear fuel reprocessing. The main thrusts of the work are briefly described here.

1. Analyzed fundamental problems in a geopolitical setting that constrain the nuclear energy sector from realizing its climate change abatement potential and suggested a plausible case-basis solution.
2. Explored a power analysis as means for knowing a priori the quality and quantity of samples required for a target predictive capability of a model. This would also allow for spectrometer equipment sizing.
3. Elucidated techniques for maximizing model accuracy while reducing false positives and preventing nefarious model confusion.
4. The speciation of Neodymium with Citrate at varying pH was observed spectroscopically. The spectral changes were then correlated with [H+] concentration, to monitor process conditions such as pH via spectroscopy.

As every nuclear reactor produces unique composition waste, the recycle make-up will be reactor specific. Thus, one research interest is being able to create robust models with multiple components, such that a recycle facility could model a multitude of reactors' fuel. Understanding modeling parameters through a power analysis would reveal how to streamline modeling and which components are viable for modeling. Finally, nuclear fuel recycling contains an array of chemical processes at varying conditions. By observing slight changes due to pH indicative of different metal-ligand products forming, UV/Vis spectra can also track important process conditions that would be indicative to normal operation and create a further tampering hurdle.

Chapter 2: Introduction

2.1: Threat of Climate Change

In the last fifty years the atmosphere has continuously absorbed massive amounts of carbon dioxide (CO_2) which has heated the earth's global average annual surface temperature by about 1.5 ^oC[1,2,3]. This may not sound substantial, but when a 5 ^oC drop was enough to put most of North America under hundreds of feet of ice[4], it becomes apparent that this small measure implies a lot of change. As this warming has been happening, scientists and activists have warned of the dire consequences. Currently, 1 million species are facing extinction due to climate change[5]. Over half of the Great Barrier Reef is dead[6]. Our largest source of atmospheric oxygen is in danger[7]. The last five years are also the five hottest years on record, in order. These are only a small sample of all the evidence pointing towards desperate straits. However, due to the efforts of gas and oil companies, along with negligent political influence to sow disinformation and confusion, this message was largely ignored and distrusted[8-14]. Now, as climate change has shifted from noticeable and damaging to unignorable and devastating, the human race will face challenges unlike anything before. Starvation, dehydration, heat stroke, and increased poverty are all guaranteed to partially destabilize society and cause significant death tolls[3,15]. Climate change will also disrupt global security and potentially instigate conflicts as it causes instability to countries and heightens tensions[16,17]. A crisis is unavoidable; but to what level the ruin reaches is not solidified, and some time remains to avoid the worst of the possible. Scientists suggest reducing global emissions by roughly fifty-percent before 2030[1] is necessary to avoid most threats to societal stability. This will require large scale economic investment in scientifically sound approaches on a multi-national level. Further, it will require investment

beyond what is economically desirable, as the free-market is not enough to drive necessary climate-change solutions. To suggest a potential solution though, we will first dig a little deeper into the problem, specifically, CO_2 as the culprit of the problem.

CO_2 absorbs incident IR radiation at 667 cm^{-1} (bending), 1338 cm^{-1} (symmetric) and 2349 cm^{-1} (asymmetric) from our sun, whereas simple diatomics such as oxygen and nitrogen do not interact with these wavelengths of the electromagnetic spectrum. Before reemitting the IR radiation, the CO_2 has an increased average kinetic energy, which causes more energetic molecular collisions, which in turn is an increase in temperature. This effect has been magnified across the atmosphere to cause a temperature increase of 1.5 ^oC over the past few decades (and now accelerating to nearly twice the heating rate of the last century), driven by the combusting of hydrocarbons as an energy source. This has been accomplished by and large through electricity generation; the combustion of fossil fuels create product gases (including heated CO_2) and heat which generates steam. The expansion of this steam powers a turbine connected to a dynamo which uses the spinning of a magnetic field to create an electric field that is the generation of electricity for civil use. After combustion, this CO_2 is useless and vented to the atmosphere. Unfortunately, the creation of CO_2 is unavoidable in many scenarios. Case examples are aviation or heavy machinery, in which it is nearly impossible to operate on batteries as the force generation is too difficult. However, electricity generation for the grid is the largest source of CO_2 production. Utilizing an alternative fuel source from hydrocarbons is necessary. Many activists are entranced by the idea of renewables due to the notion that they are largely unintrusive and emissionless. However, this is a misconception. The rare earth elements necessary for solar and wind energy require difficult and toxic chemical processes[18,19]. The CO_2

generation per quantity of energy roughly ties nuclear with wind, and vastly over solar energy[20,21]. Further, renewables require a very large amount of land compared to their energy production[22]. These factors make renewables unfavorable in many scenarios. When added to their inability to load-follow and operate at all hours of the day or in all geographical regions, a grid based on these is not viable. Nuclear energy is not tied to any of these problems however.

2.2: Utilization of Nuclear Energy

Nuclear energy is a very attractive solution to climate change, but it requires an explanation so that argument can be understood. In nature, varying number of protons changes chemical properties between elements and within each element the number of neutrons can vary, which changes the nuclear properties. One such important example is the two isotopes of uranium, Uranium-235 and Uranium-238. When ^{235}U absorbs a thermal neutron (a neutron that is in thermal equilibrium with its surroundings), the nucleus becomes unstable and fissions (splits apart) releasing fission products, neutrons, and energy[23]. The probability of the neutron being absorbed and causing this event (instead of being deflected or missing) is based on the cross-section of ^{235}U, which is a calculation based on the physical size of the atom nucleus[23]. On average, the products are 2.5 neutrons per fission event, 200 million electron volts (MeV)[23], and

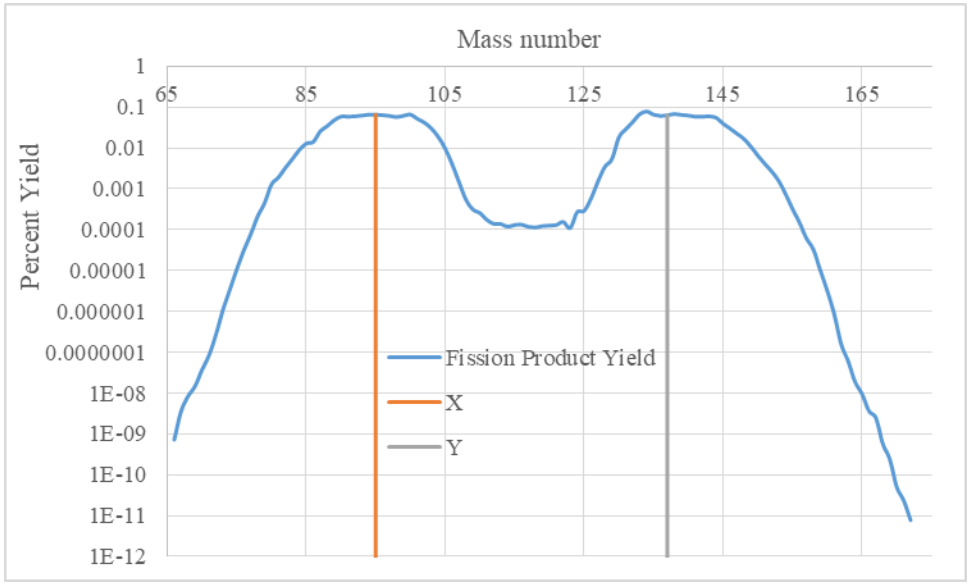

Figure 2.1. U-235 Fission Product Percent Yield by Mass Number.

a fission product X with mass number on average of 95 and Y of average 137[24] as seen in Figure 2.1. The generation of 2.5 average neutrons means the process can be sustained as a chain reaction. This defines ^{235}U as fissile.

$$^{235}U + {}^{1}n \rightarrow {}^{95}X + {}^{137}Y + 2.5\ {}^{1}n + 200\ MeV$$

Conversely, ^{238}U requires a higher energy neutron to fission, and the neutrons produced from its fission are not above the critical energy to fission an additional atom of ^{238}U, so a chain reaction cannot be sustained (outside of fast-neutron reactors which are uncommon and not discussed further). This distinction means that both ^{235}U and ^{238}U are fissionable, but only ^{235}U is fissile. Though the ^{238}U is also fertile material, meaning it can absorb a neutron to become ^{239}U and decay to ^{239}Pu, an also fissile material. This release of 200 MeV per atom (on average) means ^{235}U, enriched and burnt in a nuclear reactor will generate tens of thousands of time more energy per kg than gasoline or diesel[25]. This high energy density is why nuclear power is so attractive. As no fuel source is emissionless (renewables are commonly advertised as this but they are process emissions free; the production of the wind turbine or solar panel itself generates CO_2 emissions), nuclear energy can produce millions of more times energy on a CO_2 expenditure basis of current base-load producing methods. By utilizing nuclear energy, we can produce far less CO_2 for the same amount of energy obtained, and have a better chance of meeting climate change goals. This is illustrated by experts who have said nuclear energy is necessary to meet climate change goals, and that society will not be stable without nuclear energy[26]. A further argument for nuclear energy, arising again from its energy density, is the land usage. Nuclear energy requires a fraction of the land to produce the same amount of energy as renewables. For example, the city of Los Angeles is roughly 500 square miles, and by DoE measurements, used roughly 23 Terawatt hours (TWh) of electricity in 2016[27]. A back of the envelope calculation

using literature values for land requirement per TWh shows that to power the city of LA via nuclear energy requires roughly 4 mi^2, 307 mi^2 via solar, and 460 mi^2 via wind energy. Alongside the small area usage, nuclear energy is operable at all hours of the day. In fact, some reactors can run continuously for nearly a few years without refueling. Additionally, the power generation is set by human operation, rather than subject to nature. These traits manifest in nuclear energy being able to provide base-load power, which is the bulk of the electricity costs, without the variability. Other low emissions technology such as solar and wind are not continuously operable at all, and are very much influenced by environmental fluctuations. This restricts renewables from being able to provide base-load power, which means even if nuclear was not a better option, it would still be necessary.

2.3: Nuclear Waste, Fuel Recycling and Proliferation Threat

Though these factors make it a clear candidate for base-load generation and climate change abatement, it is not without its setbacks. The foremost is the waste. Nuclear waste is comprised of fuel rods removed from a reactor when the population of the fission products is sufficient to slow down the nuclear reaction to no longer be energy efficient[28,29]. In many reactors, this point is when the fuel is still 96% uranium, 1% being ^{235}U[29,30]. The reason the waste can still be mostly fuel but too inefficient

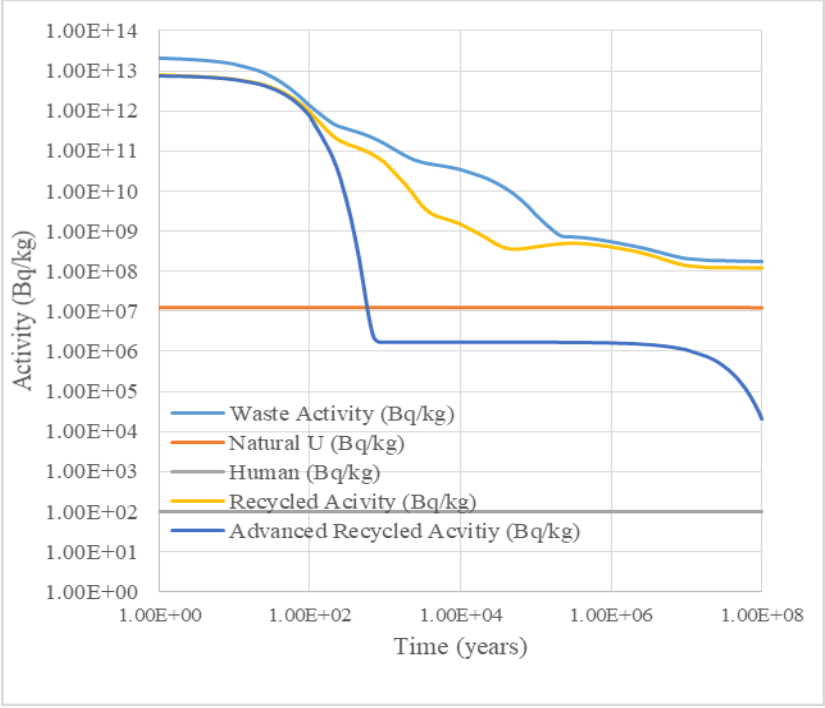

Figure 2.2. Radioactive Decay of Nuclear Material Over Time for Different Storage Practices.

to run is some fission and decay products have massive cross-sections, thus highly reducing the chance of continued nuclear reactions with $^{235}U^{28}$. The general composition of nuclear waste is depicted in the graphic below. Fission products and decay products having half-lives of thousands of years (such as minor actinide ^{237}Np with $t_{1/2}$ being 2 million years) creates a substantial problem because nuclear waste is radioactive for millions of years before it decays back to the level of natural uranium ore[29,31,32,33]. Even this benchmark point is still a hazard, but is an acceptable one. As modern civilization has only lasted a few thousand years, and the nuclear science field is hardly one-hundred years old, the notion of guaranteeing the safekeeping of nuclear waste for a million years is plausible at the very best, to arrogant and destructive at worst[33]. This problem can be solved from a scientific standpoint by utilizing advanced nuclear fuel recycling. Fuel recycling is basically the process of taking used nuclear fuel out of a reactor, dissolving the rods in concentrated nitric acid, and extracting the uranium and plutonium for reuse as MOX (Mixed OXide) fuel[29,34,35]. The remaining waste can be disposed of, while fresh fuel can be introduced alongside waste products that can be burnt within the reactor to create a recycling process. This was first developed for the weapons project, as spent reactor fuel was the best source for plutonium for bomb utilization. As detailed in Figure 2.2, the waste from the recycling is over an

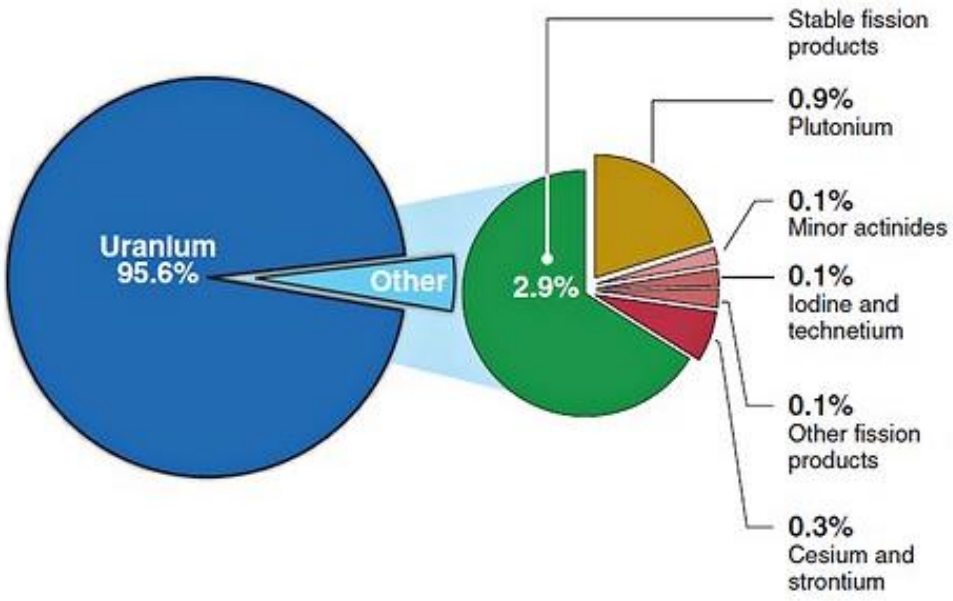

Figure 2.3 Elemental Composition of Used Nuclear Fuel.

order of magnitude less radioactive in under an order of magnitude less of time. This is a major advantage over regular waste storage in that the safeguarding does not need to be as long-lived, it drops substantially to more safe levels much sooner. It will still require eons of stewardship, but the threat is less severe in a much shorter time. This process can be expanded upon through advanced fuel recycling. Advanced fuel recycling is an umbrella term for further separations and processing after the uranium and plutonium have been recovered for fuel usage. One method under development at US DOE is the Actinide-Lanthanide Separation Extraction Process (ALSEP) which separates minor actinides Americium, Curium, and Neptunium from the waste[36]. These three isotopes, though accounting for less than 0.1% of the waste volume, account for the majority of the long-lived waste activity. They are then reintroduced to the fuel. This makes the fuel proliferation resistant as it becomes extremely radioactive and dangerous to handle, ergo theft of the nuclear material is reduced. Because it is in the fuel, during the operation of the nuclear plant it becomes exposed to a high neutron flux which will transmute the actinides into other products with (most often) shorter half-lives. This process reduces the radioactivity of the waste orders of magnitude in a very short time scale. Though the process has to be continuous (running the process generates new minor actinides in the fuel which will need to be recycled), it will localize the intense radiation to inside of a reactor and in recycling facilities, while also creating an equilibrium volume, instead of continuously accumulating. This process can be run continually with fresh fuel added to make up the loss from the burnt fuel. In the mid 1900's, this recycling (with less advanced separation) outlined a very convenient and cheap path for civilization growth. The atoms for peace program sought to hand over nuclear reactor technology along with recycling to allied countries. They could easily generate a vast amount of energy with small resource investment, and recycling their fuel drastically lowered their stewardship

obligations. This was very attractive as many countries did not possess capabilities to safeguard long-lived waste, but could more easily handle the recycled waste. In turn, by giving out the technology, the U.S. and its allies were keyed into what capabilities each country had, as well with winning favor from said country instead of the favor going to the Soviets. On the 18th of May in 1974, this strategy went up in a mushroom cloud[37]. India had been given help developing reprocessing technology along with a nuclear reactor via the atoms for peace program (specifically from Canada)[35]. India used this technology to develop fuel for a nuclear bomb, which was believed not possible at the time. This caused Jimmy Carter to ban nuclear fuel reprocessing in 1978 in the United States[38]. This created a precarious state for the U.S., as it had signed off on the NPT seven years prior. Article IV of the Non-Proliferation Treaty states

"1. Nothing in this Treaty shall be interpreted as affecting the inalienable right of all the Parties to the Treaty to develop research, production and use of nuclear energy for peaceful purposes without discrimination and in conformity with Articles I and II of this Treaty.

2. All the Parties to the Treaty undertake to facilitate, and have the right to participate in the fullest possible exchange of equipment, materials and scientific and technological information for the peaceful uses of nuclear energy. Parties to the Treaty in a position to do so shall also cooperate in contributing alone or together with other States or international organizations to the further development of the applications of nuclear energy for peaceful purposes, especially in the territories of non-nuclear-weapon States Party to the Treaty, with due consideration for the needs of the developing areas of the world."[39]

This put the U.S. in a precious situation as they wanted to discourage countries from pursuing nuclear technology, even for peaceful purposes, as it could lead to weapons development. They then quickly backtracked from civilian fuel reprocessing programs. Though Ronald Reagan

reversed this decision in 1981[40], it was only moved to an informal ban. As any entity engaged in nuclear fuel reprocessing would be denied any government assistance. As all other fuel producing entities receive government subsidies, this would lead to the company quickly becoming unprofitable. It should also be noted that nuclear energy already receives substantially less government assistance compared to other energy producers. Specifically, in 2016, nuclear energy received less than $200 million in federal funding, while renewables received almost $11 billion, and fossil fuels were given $4 billion[41]. As most nuclear power plants only developed interim storage sights, as long-term waste would be reprocessed and stored off sight, this created a problem. The long-term storage sites planned would need to be vastly larger as the waste volume would not decrease by 30% via fuel reprocessing, and also the re-engineering of the entire site was required as one-million year safeguarding instead of one-thousand year safeguarding was necessary. For this reason, there is currently no long-term fuel storage.

2.4: Conclusion

This thesis seeks to propose a solution on two fronts; political and scientific. First, research via a case-study on Saudi Arabia and their proliferation concerns seeks to find a middle ground between allowing a country to grow a nuclear energy sector while minimizing the threat of a weapons program. Second, novel techniques were explored to maximize robustness of material monitoring to safe-guard against special nuclear material theft.

The proposed solution is to invest in multinational fuel reprocessing and recycling centers, similar to the enrichment bank in Khazakstan[42]. This will provide a basis to recycle fuel at a global level, while delocalizing the capabilities, so one country does not have complete control

over the proceedings. Thus, it would be more difficult to operate a clandestine research effort for weapons development. One ideal scenario for implementation would have been Saudi Arabia, a country that has both legitimate enrichment needs and weapons concerns.

Chapter 3: Case Study for Proposed Multinational Plan for Sensitive Nuclear Technologies

This chapter was based upon research between Yeo-eun Kang and myself under the supervision of Professor Man-sung Yim as part of the Nuclear Non-proliferation Education and Research Center Fellowship at the Korea Advanced Institute of Science and Technology.

3.1: Introduction to Saudi Arabia

The global response to climate change overall will be devastating. Everywhere will see economic and physical turmoil, loss of life and resources, and harsher living conditions. However, the degree and exact nature of the problems will vary geographically. Some areas of Southeast Asia will experience extreme flooding and unrelenting monsoons while parts of the U.S. will see drought and desertification. Though both negative, these regions will have drastically different problems. Much like the results of climate change, the response will vary greatly in detail depending on region. Developing countries will have a small CO_2 output and thus less of a role in climate change abatement as compared to China or the U.S., i.e. the major CO_2 contributors. Likewise, France, largely powered by nuclear energy, is already part of the solution and less of the problem. Though overall the general solution is to lessen CO_2 output by incorporating more nuclear energy into their grid, each country will need a unique plan to accomplish this. One such very nuanced case is Saudi Arabia.

Saudi Arabia is an oil rich country in the Middle East on the Arab peninsula. The Kingdom of Saudi Arabia (KSA) holds a long rivalry with Iran. It has also developed a loose ally in the United States partly due to its large oil production and the U.S.'s oil consumption. Saudi Arabia is a very wealthy country, with a large (20k) GDP per capita. With changing dynamics in the

Middle East surrounding Iran's nuclear program, Saudi Arabia has been vocal in their concerns and adamant on being involved with the handling of Iran and their nuclear capabilities. Saudi Arabia looks to develop nuclear power infrastructure and may seek enrichment capabilities, additionally. Though there are proliferation concerns regarding all areas of the nuclear fuel cycle, many of which Saudi Arabia has yet to alleviate, this work focuses on specifically on enrichment and its proliferation potential in KSA. This focus outlines how a nuanced approach to a country can provide a more acceptable plan for climate change abatement and avoid pitfalls of taking a general blanket approach.

3.2: Saudi Arabian Nuclear Interests

Saudi Arabia wants nuclear capabilities for multiple reasons and is attempting to blur the lines such that limitations to prevent weapons could appear to be an attack against energy development. If the Kingdom of Saudi Arabia can convince the rest of the world that its power and enrichment capabilities are solely peaceful in nature, they will be allowed to have their cake and eat it too when it comes to being a nuclear-energy producing state. Therefore, it requires accurate detailing on their plans and pursuits to prevent this blurring of lines. Therefore, this section will detail Saudi Arabia's peaceful interests in nuclear energy and their merits, then examine concerns and questionable intent. This section will provide a factual basis for ideas on decreasing proliferation risk in the Kingdom of Saudi Arabia.

Currently, Saudi Arabia consumes over twenty-five percent of its oil and natural gas production for energy generation[43]. This consumption is projected to grow substantially in the coming years,

and without pursuing counter-measures (e.g. production efficiencies, further oil exploration, utilizing other fuel sources), this consumption will grow to sixty percent of KSA's fossil fuel production by 2030. Coupled with oil[44] and natural gas being the bulk share of Saudi Arabia's revenue sources, domestic consumption of resources will lead to economic ruin for the kingdom. To prevent this, Saudi Arabia has decided to pursue nuclear energy to allow for increase in oil production[45] along with development of reneweables[43,46,47]. Originally, KSA aimed to develop 17 gigawatts-electric (GWe) by 2040 produced via sixteen large-scale reactors[43,48]. However, their plans have been scaled back to two reactors producing roughly 3 GWe, potentially due to economic challenges of their original target[49]. Recently it has been discovered that Saudi Arabia has a research reactor, provided by Argentina, and expected to be operational by the end of 2019. Should they return to their original goal such as still listed on their atomic energy agency website[48], this contract would be worth close to one-hundred-billion-dollar for the development of the nuclear facilities. Currently, Saudi Arabia is entertaining a shortlist of five providers for nuclear capabilities which are China, Russia, South Korea, France, and the United States[50,51]. Aside the supplementation of oil production, nuclear energy is attractive due to its desalination potential. Saudi Arabia has no natural rivers[52] and very little fresh water sources. Consequently, KSA has very large desalination demands[53,54], and consumes a great deal of energy to meet it[53]. To this end, nuclear energy is further attractive as potentially using its waste thermal heat for desalination can be very efficient[55,56]. Thus employing nuclear energy for desalination not only lowers energy requirements overall as efficiency increases, but also incorporates a new energy source, further reducing the oil consumption for desalination. On top of diversifying their energy grid, Saudi Arabia is interested in nuclear energy to diversify their economy. Saudi Arabia wants to grow its nuclear expertise to eventually be an exporter of technology[57]. KSA also wants to

utilize their uranium ore reserves for their nuclear energy[43,58,59,60], generating wealth from a raw material outside of its large oil reserves.

Saudi Arabia's use for nuclear energy is understandable. Saudi Arabia has the largest GDP in the Middle East, largely due to its successful utilization of its oil reserves. Undoubtedly, any strategy that can free up more oil for sale (such as employment of nuclear energy) will be worth examining. Coupled with oil being a non-renewable resource, even with advances in oil extraction techniques, efficiencies in processing, and successful exploration, the country would do best by taking steps to preserve or better utilize their oil. A set-back to this argument is that, though there is economic sense of replacing oil with nuclear, there is evidence that natural gas would be even more lucrative than nuclear[61]. Though evidence shows that nuclear is more ecofriendly than oil or natural gas as far as emissions[62], that is believed not to be a motivation with KSA[45]. This, overall, casts doubt on KSA intents for nuclear energy. With an exponentially increasing population, desalination requirements will grow substantially also. Employing nuclear energy's efficiency in desalination is a very logical decision and gives strong credit to KSA's nuclear ambitions. There are questions raised around KSA's decision to grow human resources to become a nuclear technology exporter. As a country with little nuclear expertise, it will be a large time investment to catch up to current expertise, and even longer to grow some competitive advantage over other countries. Whether nuclear energy technology will remain a lucrative export over the time frame to grow this human capital is worth questioning, along with if this is the most effective investment of Saudi Arabian resources. The acceptable dimension to this decision is that by developing nuclear energy infrastructure, they will have laid the groundwork for human resource development in nuclear energy. Ergo, growing expertise for technology

exporting would eventually be achievable. Finally, the claim that utilizing their uranium ore is economically efficient is unfounded. Only initial surveys of the ore have been done to determine potential quantity. However, if this ore is suitable for mining and milling prior to enrichment to reactor grade has not been determined. Compounding this, even if it was reactor grade, it is questionable if developing an entire uranium mining sector is economical to support a small nuclear energy operation (assuming they stick to 3 GWe).

Concerns over Saudi Arabia's nuclear energy interests grow when examining their dialogue over uranium enrichment, a key step in developing nuclear energy but also nuclear weapons. Mentioned prior, Saudi Arabia is looking to negotiate a nuclear deal with several countries, however it is known that it is looking to keep enrichment rights open in its talks with the United States[43,61,63,64]. Though Saudi Arabia is not looking to begin enrichment immediately, the fact they are negotiating to keep the option on the table brings worry. This is exacerbated by the Trump Administration and its failure in taking nuclear threat as a serious issue. It is already known that there were talks to allow Saudi Arabia enriching and reprocessing technology in exchange for guarantee that American companies would be picked to build reactors. Also, the Trump Administration authorized seven nuclear technology transfers to KSA. This was all done knowing KSA has threatened to leave the NPT to create weapons to imitate and intimidate Iran. Another reason to deny KSA enrichment is that their argument to allow for enrichment lacks hard substance. Saudi Arabia has claimed enrichment will be economic for the country[57]. This is not truthful; the economics of enriching has deteriorated substantially over the last decade and are expected to continue to do so[65,66]. Pursuing enrichment does become more reasonable for programs above 10 GWe though[67]. The argument is that with substantial nuclear energy, the

economic security of controlling a larger energy source outweighs the economic burden from enrichment. But following this logic through for KSA, who is scaling back from 17 to 3 GWe (below the point this trade off makes sense), their original argument was to free up resources for economic prosperity. Thus, turning around and eating economic surplus delivered to support enrichment is counterproductive. Further, Saudi Arabia has options for reactor fuel besides enriching uranium themselves. Saudi Arabia could buy fuel from likely any supplier, as they are all seeing dwindling economic gains and would enjoy additional revenue from a new customer. If Saudi Arabia fears a lapse in their fuel supply, the IAEA fuel bank exists exactly to provide fuel, so countries do not pursue enrichment[68]. Thus, KSA is guaranteed fuel if they forgo enrichment. This all culminates in strong suspicions in Saudi Arabia's claim in enrichment as purely peaceful, which is only exacerbated by the nuclear threats made by the kingdom.

Saudi Crown Prince Mohammed bin Salman said in an interview with 60 Minutes, "Saudi Arabia does not want to acquire any nuclear bomb, but without a doubt if Iran developed a nuclear bomb, we will follow suit as soon as possible."[69] As the deputy prime minister and minister of defense, a statement of pursuing nuclear weapons from his is very serious. He also is not the only official to echo this sentiment also. Adel al-Jubeir, Saudi Arabia Minister of Foreign Affairs and former Saudi Arabia General Intelligence Directorate, Prince Turki al-Faisal, have both stated Saudi Arabia will pursue nuclear weapon capabilities if Iran attains them[70,71,72]. Fears are further exacerbated by KSA efforts to prevent intervention. Saudi Arabia has not yet signed the Additional Protocol[73] (AP) which allows for more intrusive inspections[74], nor has it signed the Comprehensive Nuclear-Test-Ban Treaty[75] (CTBT) and not only does Saudi Arabia have a Small Quantities Protocol[76] (SQP) which severely limits amount of inspection allowed in the

country, but theirs is based on the original text from 2005 which requires far less stringent reporting[77].

The information laid out previously points that Saudi Arabia clearly has viable use for nuclear energy, and unfortunately a clear willingness to pursue nuclear weapons. However, desire and willingness are very different from ability. Thus, before recommendations are made, a dialogue on potential enrichment and hence weapons capabilities, specifically their human and natural resources, is required.

3.3 Saudi Arabian Enrichment and Proliferation Potential

The enrichment process inherently has proliferation concerns; however, every country exists within its own unique conditions that can influence this threat, and Saudi Arabia is no exception. Thus, an elucidation on enrichment is beneficial as it will detail the practicality of Saudi Arabia mastering the process.

Due to many physical aspects (such as only a slight atomic weight difference[78] between isotopes) uranium enrichment is a difficult technology to develop. Gaseous centrifuges are spun to nearly one million times the acceleration due to gravity which requires not only a large amount of energy[79] but constrains materials to be both light weight and very durable. One obvious candidate that has been utilized heavily is aluminum, and hence certain aluminum exports are closely monitored and regulated by the Nuclear Suppliers Group (NSG). Unfortunately, Saudi Arabia's aluminum production is hundreds of thousands of tons annually[80]. Though a good share

of the aluminum production is for construction and building uses[81,82] which may not have the necessary production capabilities for centrifuges, the material mining and refinement processes are available. This enhances proliferation risk in KSA in that centrifuges could be built secretly without NSG detection, should the Kingdom obtain enrichment capabilities.

As detailed previously, Saudi Arabia does have substantial uranium reserves. Unlike in the energy sector, where the quality of uranium ore effects the economics of the energy produced, in weapons development, the goal is security, not financial gain. Thus, Saudi Arabia could pursue weapons development and not require an outside vendor for raw uranium ore. Of course, buying it would be cheaper than developing their own production, but by controlling it themselves, they could skew production numbers and hide their true capabilities. With KSA's current mineral industry[80] being sizeable in both mining and refining capabilities, there is potential to refine their own uranium ore, and skirt another NSG safeguard[83].

Human resources are also an immediate and imperative necessity, should Saudi Arabia pursue an indigenous weapons program. The common modality of uranium enrichment is gaseous diffusion[65,78] during which centrifugal acceleration will cause a slight separation of Uranium-235 and Uranium-238 to the interior and exterior cylinders within the centrifuge. These two gas streams flow into additional centrifuges to achieve further separation. The total arrangement of centrifuges can contain hundreds of units and are known as a 'cascade'. Further extreme care is needed to prevent leakage of the gas product, due to both the gaseous uranium hexafluoride having a high chemical toxicity[78] and the value of the enriched uranium. This culminates in the successful development of an enrichment process requiring high precision engineering and

science[78,83,84]. Saudi Arabia does not yet have substantial nuclear manpower but are currently growing it[57]. Currently receiving assistance from Argentina, it is in the process of training reactor operators. Literature searches do reveal that there is significant expertise in chemical diffusion in KSA, however it is generally focused around water desalination. Further, KSA has reached agreements with both China[85] and South Korea[86] for development in human resources and nuclear capabilities. Specifically, China will help Saudi Arabia develop its nuclear regulatory program, production of high-temperature gas reactors (HTGR), and most importantly, it's intellectual property[85]. South Korea and Saudi Arabia have focused on helping KSA develop both SMART technology (SMART technology is a type of Small Modular Reactor, or SMR) alongside human resources in nuclear capabilities[86]. Though these technical capabilities are vastly different from uranium enrichment, they show that Saudi Arabia can achieve both importing nuclear technology and intellectual capability. These factors suggest KSA can overcome the difficulties in enrichment and obtain a program, should they choose to pursue it.

The last resource of note here is economic. Outside of technical difficulties, a huge barrier to nuclear weapons development is the cost[88,88,89] (though North Korea has bucked the trend[90]). With a GDP over $600 billion[91] and billions of barrels of oil reserves[92], Saudi Arabia is a rather wealthy country. They could thus develop a weapon program, whether a more conventional or a North Korean styled route.

The summation of Saudi Arabia's enrichment and thus proliferation potential is that its plausible. The kingdom possesses resources such as uranium and aluminum which could be quite

exploitable for indigenous development of enrichment without detection. Also, though indigenous development is rigorous and costly it is not impossible for the kingdom.

3.4 Viewpoint Interpretation of Information

For ideas to gain support and stimulate healthy discourse, they not only require a strong factual basis, but an understandable and realistic interpretation of the facts. Here, the previous section shall be examined for a speculation on potential and likely outcomes.

Examining the situation in full, Saudi Arabia is truly posed to prosper from developing nuclear energy, and honestly wants to. With the Kingdom's large desalination requirements, utilizing the efficiency of nuclear energy for this process is naturally attractive. Further, by establishing nuclear powered desalination, KSA frees up oil consumption to be exported instead of consumed domestically, generating more wealth for the country. The economic gain is further advanced by a nuclear sector, should Saudi Arabia follow through with plans to be a reactor technology exporter and thus further diversify their economy. These desires are echoed in some of KSA's actions in the nuclear field. Establishing a regulatory committee[85,90,93] is arduous and would be a waste of time and resources should Saudi Arabia not truly hope to build a nuclear energy program.

The true worry is that Saudi Arabia truly desires nuclear energy and is also wanting to take advantage of their program to become a latent nuclear weapon state[61]. Saudi Arabia likely does not fully want to commit to a weapons program[61,94,95] that is both costly and dangerous.

Undertaking nuclear weapons development would exhaust large amounts of recourses, further destabilize the region, heighten global tensions, strain or even eliminate alliances, and potentially put KSA in the crosshairs of sanctions. One expert asserted, speaking on their want to develop weapons to threaten Iran, "..if they want to imitate Iran, then they should no longer be regarded as an ally of the United States." As the Senate resolution to end the war in Yemen drew President Trump's first veto, relationships are already strained between the two countries. However, Saudi Arabia's behavior indicates that they want a nuclear option. Plenty of statements by Saudi Arabia itself[69,72] indicate a willingness to pursue weapons which seem to be more than boasts or threats. Saudi Arabia has pursued agreements with the United States to keep open their enrichment rights[50,57,59,64,96], should they buy nuclear technology from the U.S. The contents of the agreement talks have not been fully diverged but is quite worrying[97,98], and to quote Congresswoman Ileana Ros-Lehtinen, "Unfortunately, from the little we do know from the Administration, it is looking at this deal in terms of economics and commerce, and national security implications only register as a minor issue, if at all."[99] This shows serious concern over the potential for Saudi Arabian proliferation. Admittedly, Saudi Arabia has consistently said it wants the option open, not necessarily start immediately, but this is hardly comforting, as the logic does not show they would keep the option open without trying to engage in enrichment. This conclusion stims from multiple behaviors. As mentioned, they have claimed their uranium is economical to extract and enrich. Even if the ore is reactor grade, it would not be economical to enrich, and they have not even proved it is reactor grade. Further, as they have shied away from initial plans of 17 GWe, extracting uranium would be way below the threshold for enrichment to be desirable from an energy security perspective, which hints at ulterior uranium utilization plans, such as weapons. These concerns also arise from KSA's lack of adherence to

certain nonproliferation regimes. As mentioned earlier, KSA has yet to modify its SQP, sign the CTBT or sign the AP. Though they have signed the Treaty on the Non-Proliferation of Nuclear Weapons[100] (NPT), this is largely seen as insufficient, especially for a country seeking nuclear energy capacity. This gives concern that KSA wants the ability to go undetected, should it pursue weapons capabilities.

Based on information laid out, it appears Saudi Arabia wants to have its nuclear power and keep the option to develop weapons too. Saudi Arabia is largely suspicious of Iran[101], and because Iran is years ahead of nuclear technology development, Saudi Arabia feels pressured to match. Since successful development of a weapons program takes years, if not decades, Saudi Arabia is pushing to develop as much of a nuclear field without actually developing weapons. Thus, if or when Saudi Arabia feels it needs nuclear weapons, they will not be years out from obtaining them. Simply put in meteorological terms; Saudi Arabia is a nuclear weapons watch, but not a warning.

3.5 Recommendations to Impede Saudi Arabian Proliferation

3.5.1 No Context Recommendation

The foremost recommendation is that Saudi Arabia signs the AP and revokes its SQP, regardless of any other action. Whether KSA increases their target to 17 GWe or not, abandons their enrichment option, etc., it is necessary to have an AP to allow for IAEA inspections and verification along with not having an SQP. In the SQP version in force in KSA[76], reporting is not required up to 2 lbs. of plutonium[102] and KSA does not have to reveal the development of a

nuclear facility until only on 180 days prior to introducing nuclear material. This lack of reporting was shown to be an obvious problem when it was discovered KSA already has a research reactor facility underway, that could be operational within the year. With the SQP revocation, should Saudi Arabia pursue nuclear proliferation, the distance from violating their agreements to achieving nuclear weapons is more daunting, and proliferation is more strongly discouraged. This discouragement would be enhanced by signing the AP, which would allow for more strict verification. Note should be made that KSA should sign the Model Additional Protocol, i.e. not having provisions that weaken verification and monitoring capabilities, as was the case in India[61]. Finally, Saudi Arabia should sign the CTBT. This will create further legal obligation for KSA not pursue weapons, as weapons testing is seen as a vital aspect of weapons development. The Kingdom may have an initial response that they do not want weapons, therefore they do not need an agreement against testing; however, KSA has stated interested in a nuclear weapon free middle east[95]. Assistance towards this goal could be a bargaining point for their CTBT signing. These recommendations would all prove helpful in preventing proliferation in any path Saudi Arabia and are suggested alongside any of the subsequent scenarios listed below.

3.5.2 No Enrichment within Saudi Arabia

With the current plans remaining at 3 GWe of nuclear energy, Saudi Arabia must not receive agreements to allow for enrichment. Enrichment is already uneconomic, as detailed above. Especially if the Kingdom keeps its nuclear capacity at 3 GWe, it is illogical to develop an entire enrichment facility when cheap fuel is readily available on the current market. If Saudi Arabia

does switch back to a 17 GWe (or any target above 10 GWe), it is still suggested to pursue Saudi Arabia forgoing enrichment. To enhance the attractiveness of this recommendation, multilateral fuel arrangements can be made. Foremost, a contract with more than one country to provide the nuclear fuel would reduce the leverage over KSA their fuel suppliers would have, as another country could switch from partial to total contract fulfillment. Seeing as KSA is in talks for reactor technology from multiple countries which could provide nuclear fuel[65,78,103,104], they could include terms about fuel procurement in the reactor purchase. A multilateral agreement between the fuel provider(s), KSA, and the IAEA to keep a set amount of fuel for Saudi Arabia on hand at the IAEA international fuel bank in Kazakhstan would strengthen this agreement. Keeping the fuel on hand in KSA is suggested against as their current behavior makes them a proliferation worry, and minimizing their nuclear material is desirable. But also, by having the fuel out of the hands of the provider, it removes Saudi Arabia's fears over energy security. Finally, another resource exists in the International Uranium Enrichment Center (IUEC) in Angarsk, Siberia[65,96]. Saudi Arabia could seek membership to the IUEC, which could provide them enriched fuel without giving them enrichment technology.

3.5.3 Allowance of Multilateral Saudi Arabian Enrichment

Should attempts to outright forgo enrichment fail, Saudi Arabia should agree to a limited enrichment program. Limitations should come in the form of both stewardship and capacity. Any agreement to keep open Saudi Arabian enrichment rights should come with compromises that any facilities are not solely built, owned, or operated by KSA. The level and nature of foreign ownership and operation is not analyzed here as it would require coordination of contractors,

Saudi Arabian representatives, and others. But obviously, the less control KSA has, the better. Having partial foreign ownership and operation of the facility will heighten the scrutiny of their enrichment. Though nonnatives would not be involved in safeguards and verification, they would be involved with mass balances, sales and distribution which would limit Saudi Arabia's freedom to divert material unannounced. For construction and operation of facilities and technology, as much as possible should be 'black-boxed', i.e. Saudi Arabia given no sensitive information or data on the process. This will require larger difficulties in reverse engineering centrifuge technology. There remains the threat of if Saudi Arabia was to kick out operators and assume complete control, they could eventually attain weapons grade uranium. Again, this becomes unpreventable if enrichment within Saudi Arabia is allowed which is why the previous recommendations are safer and more desirable. But to at least slow this process and discourage it, which would give sanctions and political intervention more time to act, the enrichment capacity of any facilities should be limited.

Limitations on Saudi Arabian enrichment capabilities would strengthen the confidence in KSA not pursuing enrichment for weapons by enhancing the difficulties associated. Limiting uranium enrichment capabilities to a narrow operating regime would make energy security a sacrifice for weapons development, which would be a large disincentive to KSA. To recommend reasonable limits on enrichment, an understanding of Saudi Arabian power needs is necessary. First, the assumption is made that the enrichment is allowed due to KSA going above 10 GWe in enrichment for reasons discussed above, so a model case of KSA growing from 3 to 17 GWe nuclear is used. As Saudi Arabia has not yet decided on a supplier or design for its reactors[50,51], the burnup of 55 Gigawatt-day per metric ton of uranium (GWd/MTU) is used, which is close in

value to an APR1000, representing an example of current reactor technology. Regardless of cascade or centrifuge design, the separative work unit (SWU) per mass basis follows Equation 1 [79]. SWU is the work required, P is the mass flow of the product (enriched stream), T the mass flow rate of the tails (depleted uranium), and F the mass flow rate of the feed (natural uranium). The value function, V(x), is based on the concentration (x) in mole fraction of the stream and follows Equation 2[79].

$$SWU=P\cdot V(x_P)+T\cdot V(x_T)-F\cdot V(x_F) \quad (1)$$

$$V(x)=(1-2\cdot x)\cdot \ln((1-x)/x) \quad (2)$$

Basic reasonable assumptions are made to outline production requirements for Saudi Arabia. First, they would not likely start production on all plants simultaneously, as their power needs are expected to grow, they will grow production with it; taking time to produce their full nuclear fleet will also prevent a rapid consumption of economic resources. A decade was chosen as a reasonable period for the additional nuclear capacity to come online. Second, as experience breeds efficiency, a slight exponential curve to the power generation is applied, as facilities would come on-line quicker. Third, as the original plan was 17 GWe from sixteen large scale power plants, roughly 1 GWe per power plant is used. Fourth, as all current SMR plans are for under 100 MWe, they contribute little to the requirement for fuel. Fifth, as shutting down an enrichment cascade is quite undesirable (as achieving steady-state equilibrium for the separation is very difficult[65,79]), it is more reasonable to keep cascades running continuously, thus added enrichment capacity is via new cascades that can be installed independently, rather than expanding current cascades. Further, calculations are made based off cascades of 90 machines

with an average SWU of 300 per machine[79], such as in an AC100 design. This is chosen as AC100's are made from composites that are not produced in KSA, so should the country reverse engineer the design, they would need to modify it for aluminum or still seek outside help for fabrication. Finally, fuel stream conditions are specified based on industrial norms of 0.7 percent for the feed via natural uranium, 0.1 percent tails[65,79] for U.S. standards, and 4.8 percent fuel, as specified from Saudi enrichment desires for SMART units[65]. This will require an obvious necessity of material accountancy in the tails, product, and feed. Further, limitations on the centrifuge operation via software and/or mechanical constraints are suggested, though the method of implementation for those constraints likely lie outside of public knowledge.

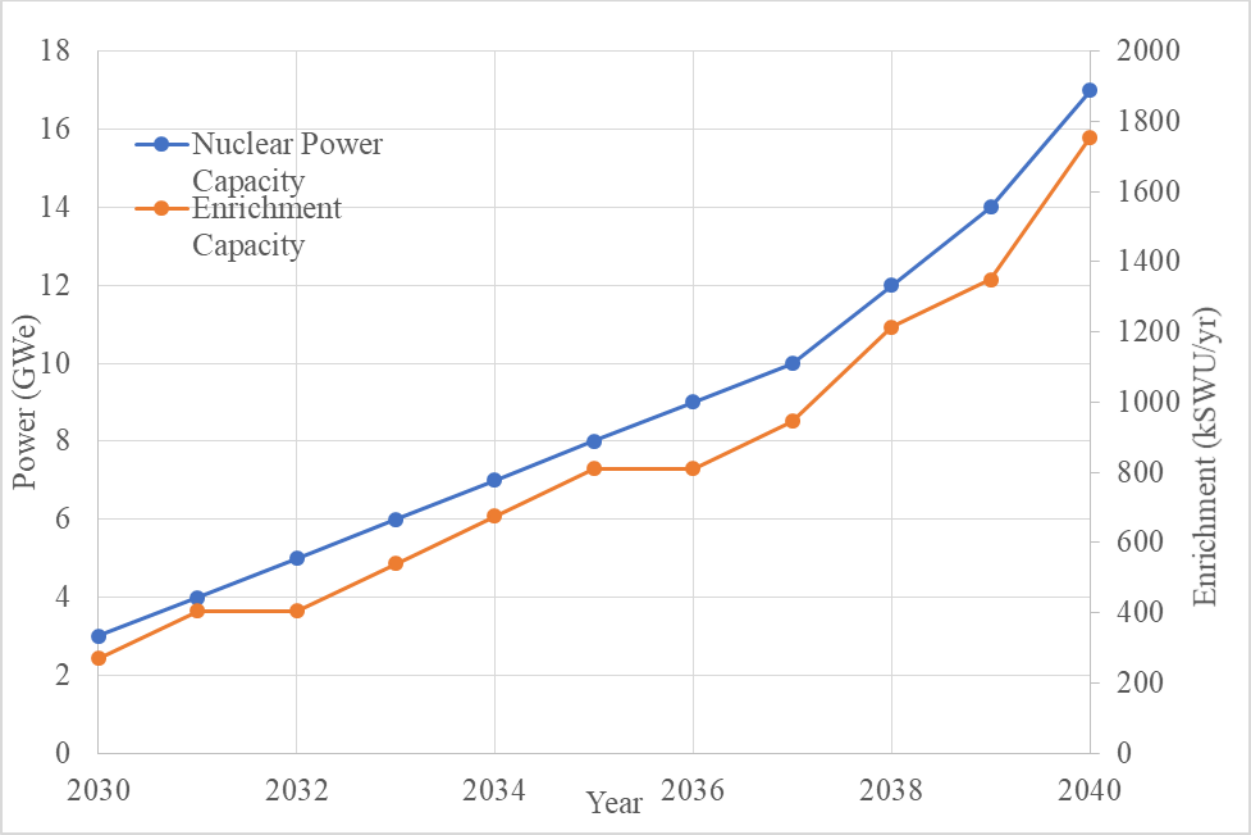

Figure 3.1. Nuclear Power Generation Increases as 17 GWe is Achieved Over a 10-year Period. Enrichment Capabilities Increase Over the Same Window.

Using both assumptions and known values, a limitation on enrichment capacity is generated such that domestic production never exceeds eighty-five percent of consumption. The argument is that by keeping production below consumption, they are always required to seek additional enrichment sources out of their control. Thus, to pursue higher enrichment for weapons, they will either forgo part of their own enrichment needs, causing turmoil via power lapses, or increase purchases which can be monitored internationally. Figure 1 details the increase of nuclear power capacity in GWe and a trailing enrichment capacity in kSWU/yr. Equation (1) and (2) allow for calculation of kSWU/yr required to meet energy demand. This is shown in Figure 3.2 where also a near constant amount of enriched fuel is imported. In Figures 3.1 and 3.2, it is clear enrichment capacity does not grow linearly with capacity, nor is imports constant. This is due to cascades being installed in unit intervals as shown in Table 3.1, so the increase in a production cascade can only happen when it will not bring production to over eighty-five percent of fuel needs. In years where fuel demand increases more than production is allowed, imports increase as seen in Figure 3.2. Effort was taken to also keep imports as roughly constant, as supplier companies would prefer steadier income. To allow operation of a centrifuge facility in 2030, construction should start as late as possible such that down-time does not happen or is minimized. Further, the facility should be built to accommodate future cascades, though cascades themselves are not installed or operated until the given year specified in Table 3.1. It is assumed 2040 would be the steady-state conditions for the facility.

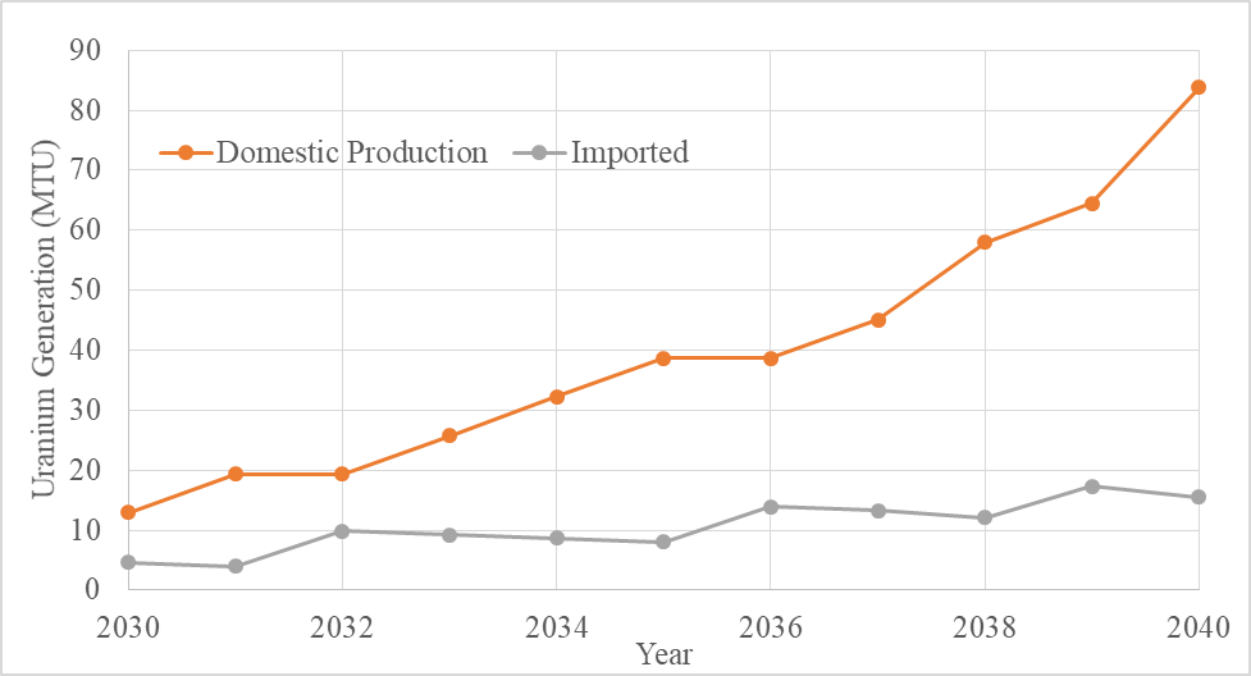

Figure 3.2 Domestic production of enriched fuel increases with demand. A roughly constant amount is imported to supplement domestic production.

This capacity lay-out is not the only viable option; rather a suggestion of one possible option and explanation of the logic such that it could be recreated, should conditions change. Certainly, if the timeline, energy target, or reactor design (thus fuel requirements) change, all these calculations would need to be redone. Also, calculations would change based on centrifuge and cascade design, as well as product and tails specifications. Additionally, this solution does not guarantee nonproliferation, but is to merely slow down the proliferation process and increase the opportunity cost, should Saudi Arabia engage in it.

3.5.4 Saudi Arabian Sole Enrichment

Should Saudi Arabia receive sole guarantees for sole ownership and operation of any domestic enrichment facilities (a worst-case scenario), at the very least, capacity limitations should still be imposed. Though even with such limitations, it would be assumed over time Saudi Arabia would acquire weapons grade uranium to. This is undesirable, and only suggested if it is believed Saudi Arabia will develop uranium enrichment regardless, so at least the timeline of weapons grade uranium procurement is known. Thus, the same process condition restrictions listed above are suggested. This scenario is not evaluated further as it would evolve into descriptions of direct interventions, sanctions, and other avenues beyond the scope of this research.

Proposed enrichment capacity conditions					
Year	Enrichment Capacity (kSWU/yr)	Product (MTU/yr @4.8% U235)	Feed (MTU/yr @0.7% U235)	Tails (MTU/yr @0.1% U235)	Cascades of AC100
2030	270	16.8	169.6	152.8	10
2031	405	25.2	254.4	229.2	15
2032	405	25.2	254.4	229.2	15
2033	540	33.6	339.2	305.6	20
2034	675	42.0	424.0	382.0	25
2035	810	50.4	508.8	458.4	30
2036	810	50.4	508.8	458.4	30
2037	945	58.8	593.6	534.8	35
2038	1215	75.6	763.2	687.5	45
2039	1350	84.0	848.0	763.9	50
2040	1755	109.2	1102.4	993.1	65

Table 3.1. Specifications of centrifuge operation conditions during ramp up period.

3.6 Conclusion and Policy Implications

Saudi Arabia is a unique growing proliferation concern. Its need for nuclear energy makes denial of nuclear technology impossible and unethical, however its threat of nuclear weapons creates a grave concern for the dual use nature of this technology. Stringent care needs to be taken with whatever technology is and has been granted and in what form or to what extent. First and foremost, signing of the AP, CTBT, and revoking their SQP is strongly suggested. By adhering to these international safeguard regimes, Saudi Arabia will show proof in their claims of desiring only peaceful nuclear capabilities while also allowing limiting any covert actions. Denial of nuclear enrichment agreements is an obvious choice but will require further negotiating to give KSA confidence in their energy security. This can be done by utilizing the multinational fuel banks or enrichment center to ensure fuel supply. If KSA is not dissuaded against pursuing enrichment, Saudi Arabian ownership, operation, and technological know-how should be minimized. Further, limitation of their enrichment capacity will reduce future proliferation desires as it creates further obstacles. Nuclear proliferation is a concern with Saudi Arabia, and assuredly controlling enrichment is a key to preventing both proliferation and reducing nuclear weapons latency.

Acknowledgements

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Chapter 4: Theoretical Foundation

The policy recommendations described previously examine only a small aspect of the fuel cycle (mining, fuel fabrication, reactor operation, reprocessing and storage were not examined) of one country. However, it serves to show that each country will present unique challenges that need examining in full to prevent nuclear weapons proliferation. One serious problem that will arise in any country's nuclear fuel cycle is recycling and storage. Regardless of any geopolitical factors, a final repository will have serious concerns simply on the inherent time scale of the threat. Recycling is a practical and logical conclusion from a scientific stand-point but contains many political drawbacks. A fully developed solution to the inherent safety threats of recycling is beyond the scope of this thesis. However, this thesis can contribute towards the solution, and the remainder aims for exactly that. The rest of this work is involved in the development of a safeguarding system to monitor special nuclear material using simple techniques that would be low cost and easily reproducible. Previous research has already established UV/Vis spectroscopy as being capable of monitoring material[105-108]. This chapter will outline the theoretical fundamentals which provide the basis for the experimental sections of this work and thus the rest of the thesis.

4.1 Chemometrics

The underlying physics which governs the system modeled and analyzed in this work is spectroscopy. Specifically, spectroscopy of the Ultra-Violet(UV) and Visible (Vis) spectrum, or UV/Vis. This is the measure of absorption of light from wavelengths from roughly 200 to 1100 nm. The research chose UV/Vis as this is a region of the spectrum that many actinides and

lanthanides that are found in nuclear waste have absorption signatures, such as U and Pu. The process of absorbance occurs when light of these wavelengths excites electrons of atoms at a specific vibrational frequency, and the electrons absorb the energy from the photons which is converted to internal energy. For example, in Nd, the hypersensitive peak is around 578 nm and for Ho at 453 nm[109,110]. These hypersensitive peaks are specifically 4f electrons for lanthanides being excited and refer to transitions that are very sensitive to changes in the electron's environment due to they follow electric-quadrupole selection rules while also having a total change of angular momentum less than two[111,112,1113]. These electronic conversions of energy are spectroscopically observable and modelable. The absorbance of light is calculated as the negative log of the ratio of final and initial intensity of light transmitted.

$$A = -log_{10}\left({I_T}/{I_O}\right)$$

The probing of chemical systems and utilizing mathematical or statistical models to understand such systems is known as chemometrics. Much of the practicality of chemometrics is due to the linearity of the Beer-Lambert Law.

$$A = \ell \sum_{i=1}^{N} \varepsilon_i c_i$$

The Beer-Lambert Law requires six conditions to be valid. They are 1) Attenuators (absorbing species) must be independent from one another; 2) The solution must be homogenous across the light path; 3) The solution must not be turbid (meaning the species must not scatter light); 4) The incoming light rays must be parallel while traveling through the solution; 5) The light needs to be monochromatic; 6) The light cannot induce reactions or electronic transitions. The power of the Beer-Lambert law in chemometrics is that it describes a linear relation between absorbance and

concentration. Because the goal of the research is to create linear models, it is a prime candidate system for the research.

4.2 PLS Modeling

Before models are generated, data generally undergoes preprocessing to maximize the predictive ability of the model. Though there are numerous preprocessing techniques which can be used in many permutations, this research utilized autoscaling for the data. Autoscaling is the process of subtracting the mean from each variable then dividing by the standard deviation. The result is variables of mean-zero and a standard deviation of one. The advantage of autoscaling variables is it will normalize the baseline across samples; some samples may require individual baseline correction within a sample though that is not handled via autoscaling. By dividing by the standard deviation, all variables can be weighted the same, such that their variance influences the model more so than their absolute value. Figure 4.2 below illustrates an example data set before and after autoscaling.

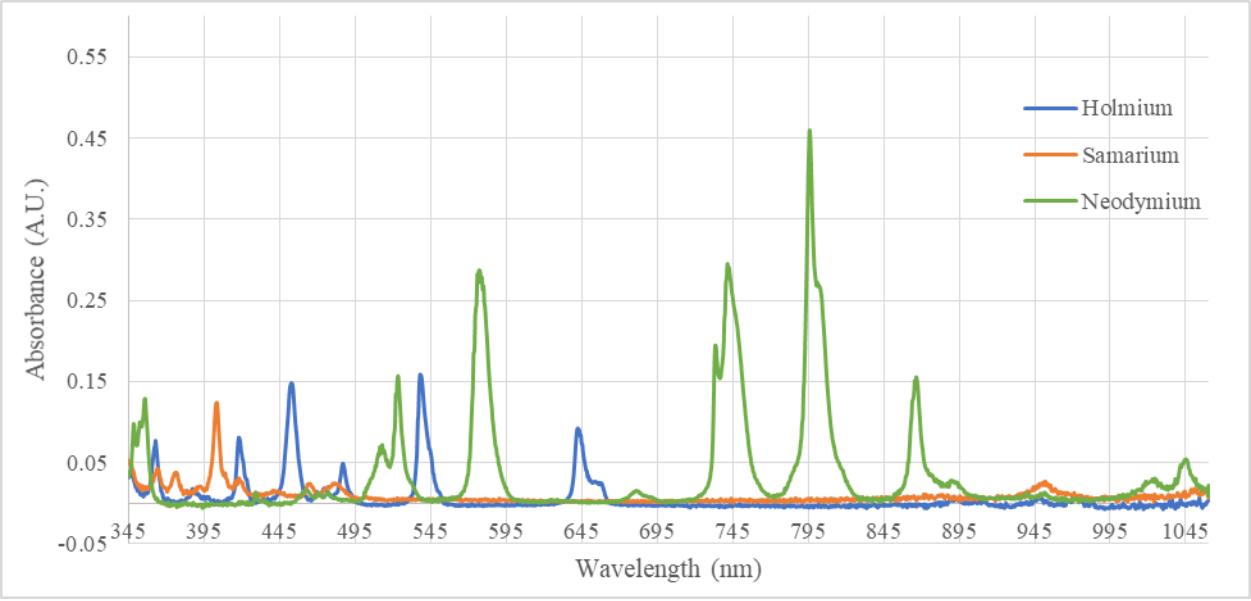


Figure 4.1. Representative Spectra of Data of Holmium, Samarium, and Neodymium Samples.

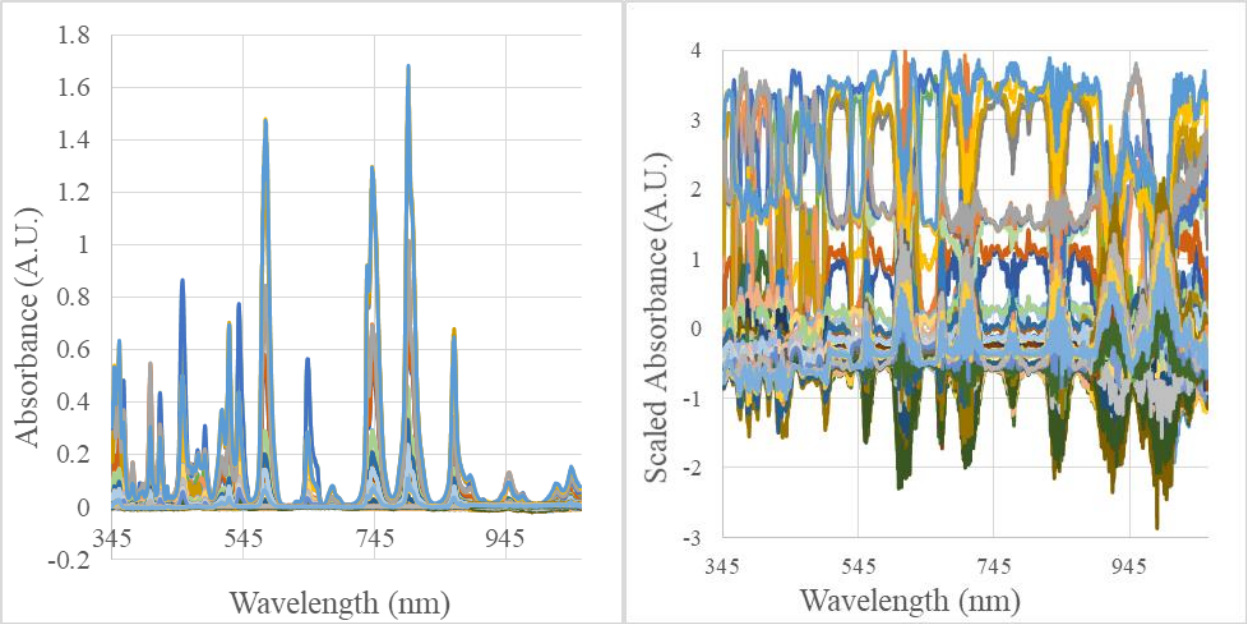
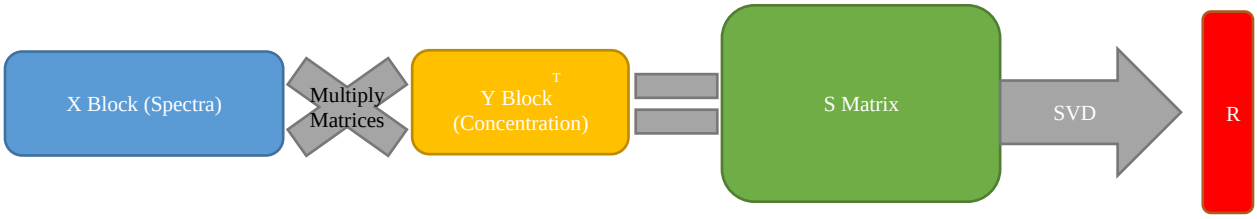


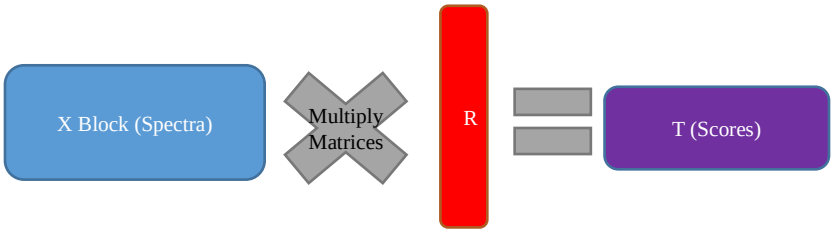
Figure 4.2. Change from Raw to Preprocessed Data of Varying Concentration Holmium, Samarium, and Neodymium Samples.

The models generated in this work are generated through the method of partial-least squares (PLS). Partial least squares is a regression method in which data from a predictor matrix (Y) with samples listed down the y-axis and variables down the x-axis, and a response matrix (X) of equal design, are both projected to a single space to maximize the covariance of the two previous spaces[114,115]. In more traditional least squares solutions for a system of design $\boldsymbol{Y=XB+E}$ where $\boldsymbol{B=(X^TX)^{-1}X^TY}$. This is problematic in spectroscopy due to the collinearity of spectra. Collinearity is when multiple variables are highly correlated but not necessarily linearly dependent. This is the case in spectroscopy due to the absorbance at neighboring wavelengths being a product from the same electron excitation. This collinearity generally leads to $\boldsymbol{X^TX}$ being singular, implying the inverse $\boldsymbol{(X^TX)^{-1}}$ does not exist[114]. PLS regression circumnavigates this inverse deficiency by decomposing $\boldsymbol{X}$ into orthogonal scores and loadings called T and P

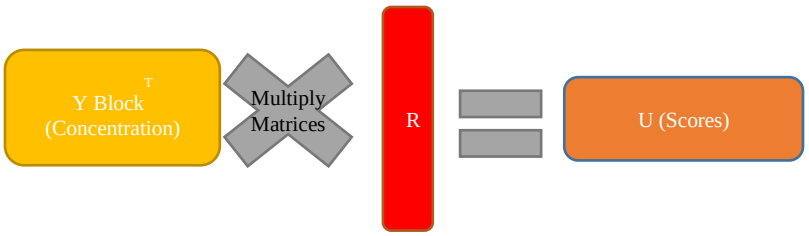
respectively, such that $\boldsymbol{X=TP^T}$[115,116]. Then the Y matrix is regressed onto the first columns of the ***T*** scores, where the number of columns chosen is the number of latent variables (LV's) for the model. In other regression methods, such as PCR, the variables are chosen in order of decreasing variance captured in X[117]. However, as PLS maximizes covariance of ***X*** and ***Y*** blocks, the LV's are ordered via decreasing covariance. One key advantage of PLS regression over other regression methods is it incorporates information from both ***X*** and ***Y*** blocks[115]. This is done specifically to maximize the covariance of the two data blocks. The covariance of ***X*** and ***Y*** is the correlation multiplied by the standard deviation. A mathematical representation is $\boldsymbol{cov(X,Y)=E[(X-E[X])*(Y-E[Y])]}$, where E is the expectation value. A more intuitive (but less practical due to loss of significance) is $\boldsymbol{cov(X,Y)=E(XY)-E(X)E(Y)}$. A general blueprint of the process of PLS is shown below. Another advantage of PLS-R is by using covariance, the output is in units of ***X*Y***, which for models handled in this thesis are units of concentration, an easily interpretable output.



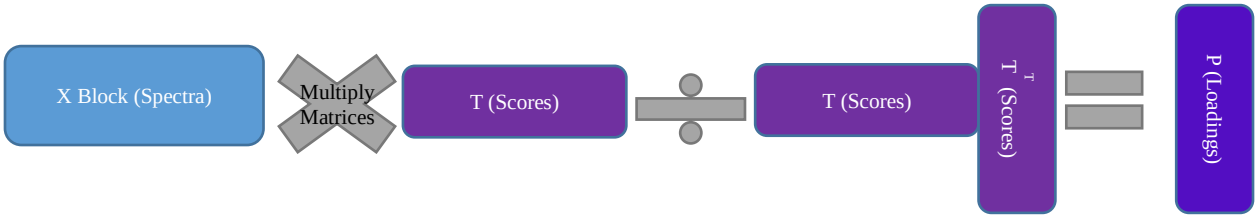
4.3 A. Raw Data Matrices Multiplied to Create Covariance Matrix (S), Then Decomposed Into Singular Values (R) via Singular-Value-Decomposition.



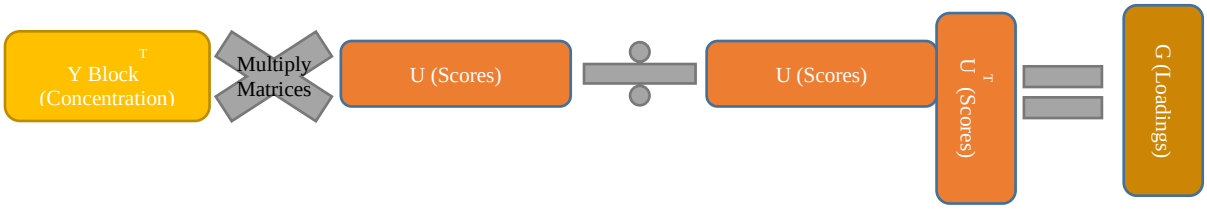
4.3 B. X Block Multiplied by Singular Vector to Create Scores (T) to Capture X Block Sample Variance.



4.3 C. Y Block Multiplied by Singular Vector to Create Scores (U) to Capture Y Block Sample Variance.



4.3 D. Loadings (P) Capturing X Block Sample Variance is Created from X Block and Scores.



4.3 E. Loadings (G) Capturing Y Block Sample Variance is Created from Y Block and Scores.

Figure 4.3. Schematic of PLS Algorithm.

PLS-R maximizes the covariance of the ***X*** and ***Y*** blocks via the SIMPLS algorithm. The SIMPLS algorithm was developed in 1993 for PLS-R[115]. It is detailed in brief below.

For each $h=1,\ldots,c$ where $A_o=X'Y$, $M_o=X'X$, $C_o=I$, and c is given (the chosen number of latent variables),

1. Compute $\mathbf{q_h}$, the dominant eigenvector of $A_h'A_h$
2. $w_h=A_hq_h$, $c_h=w_h'M_hw_h$, $w_h=w_h/\sqrt{c_h}$, then store w_h as columns of W
3. $p_h=M_hw_h$ and store p_h as columns of P
4. $q_h=A_h'w_h$ and store q_h into columns of Q
5. $v_h=c_hp_h$, $v_h=v_h/||v_h||$

6. $\boldsymbol{C_{h+1}=C_h-v_hv_h'}$, $\boldsymbol{M_{h+1}=M_h-p_hp_h'}$
7. $\boldsymbol{A_{h+1}=C_hA_h}$

The major advantage of the SIMPLS algorithm is the covariance matrix of $\boldsymbol{X}$ and $\boldsymbol{Y}$ is deflated, instead of the $\boldsymbol{X}$ and $\boldsymbol{Y}$ matrices being deflated individually. This is specifically of interest because it guarantees the allowance of different $\boldsymbol{Y}$ variables (metals) correlating to the same $\boldsymbol{X}$ variables (wavelengths). Whereas in the NIPALS algorithm (the dominant PLS-R algorithm before SIMPLS), deflation of the blocks separately creates the possibility of correlating only a single $\boldsymbol{Y}$ variable to a specific $\boldsymbol{X}$ variable[115].

After creating PLS models, they are inspected via their summary statistics. Primarily, statistics like Root-Mean-Square Error of Calibration and Cross-Validation (RMSEC & RMSECV) are good indicators of performance, though the RMSEP is more useful[116,117]. The RMSEP utilizes the full training set, alongside having a unique test set, thus is more accurate for validation purposes. Additionally, statistics such as Q-values and Hotelling's T^2 are utilized to verify a well-behaved model. To understand them, first requires understanding of the full errors. In a standard linear regression, some $\boldsymbol{X}$ block of data (absorbance in the case of this research), is decomposed into three matrices.

$$\boldsymbol{X = TP^T + E}$$

where $\boldsymbol{T}$ is the scores which describes relationships between samples, $\boldsymbol{P}$ is the loadings which describe relationships between variables, and $\boldsymbol{E}$ is the estimated errors. In the Beer-Lambert law, these scores will elucidate the molar attenuation coefficients, since per variable, those are what change across samples, while the loadings will describe the concentration, since across

wavelengths, the concentrations are what are consistent[114]. The errors from electronic noise are used to compute Q-Residuals via

$$\boldsymbol{Q_i = e_i e_i^T = x_i\left(I - P_k P_k^T\right)x_i^T}$$

where $\boldsymbol{e_i}$ is the element in the i^{th} row of the errors E, P_k is matrix of retained loadings in the model where each column of $\boldsymbol{P_k}$ is a vector in the model and x_i is a row (sample) in the $\boldsymbol{X}$ predictor block[117]. Q-residuals give an estimate of how well each sample fits the model. Thus, when looking at the Q-residual of a given model, a poor performing sample can be removed, or if sufficient samples have large Q-residuals, the model can be expanded. Of equal use is Hotelling's T^2, defined as

$$\boldsymbol{T_i^2 = t_i \lambda^{-1} t_i^T = x_i P_k \lambda^{-1} P_k^T x_i^T}$$

where $\boldsymbol{t_i}$ is the ith row of the scores matrix in the model, and $\boldsymbol{\lambda}$ is the diagonal matrix containing the eigenvalues of the latent variables[117]. If a model is considered as a best fit line through a set of data, the Hotelling's T^2 (T^2) can be thought of as the distance from the center of the model in the plane, and Q values are the distance from the line out of the plane. Figure 4.4 below helps depict this.

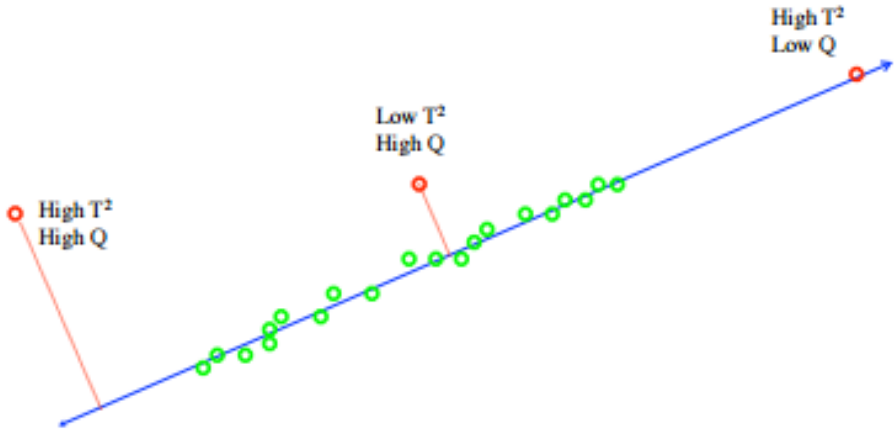


Figure 4.4 PLS Summary Statistics and Their Model Relation. Provided by Wise, B., Gallagher, N., and Roginski, R.[114]

With the description above, it becomes clear that T^2 is a measure of the leverage of a data point. Higher T^2 implies a higher weight on the model than other data points. This is not necessarily a bad thing; some data points could be more important than others. However, it requires careful inspection that the high T^2 are good data points with low errors, or it will influence the model poorly[117]. Conversely, Q values are the distance from the line to the data point. High Q values are not good because they generally imply the data point is behaving according to another variable not being captured by the model. Sometimes this is a result of not using enough latent variables, and is a simple fix, though it can also indicate a sample was poorly made or influenced by another factor. An example is shown in Figure 4.5. There exist samples with both high Hotelling's T^2 and Q-Values, however, no samples have both. The samples with high Q-Values have low T^2, implying the samples that are not modeled well are not contributing largely to the model, and the sample with large T^2 (and thus a large influence), have a low Q-value indicating they are properly modeled. The ideal case would be samples with no high Q or T^2 values, however, no samples with both is still acceptable.

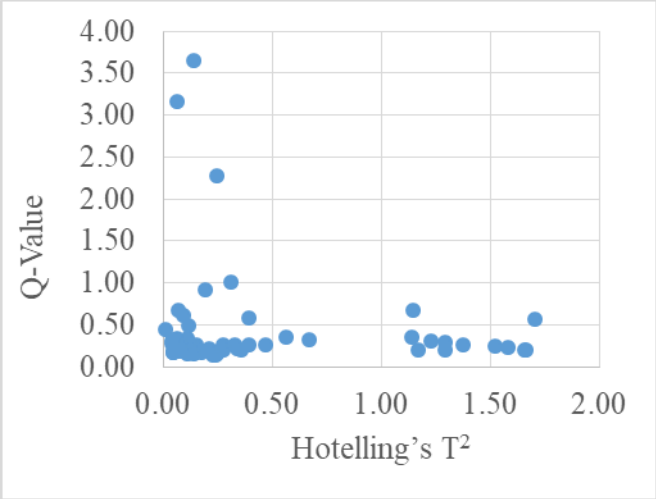


Figure 4.5. Sample of Summary Statistics for an Acceptable Model.

4.3 Power Analysis

In chronological order of this thesis, a preliminary study into the neodymium-citrate speciation was done. As described further below, the results were inconclusive; the errors were far too large. Though mainly due to the speciation experiment being done via series dilution (thus the

signal to noise ratio decreasing greatly), the spectral shifts due to speciation were too small for accurate modeling. Literature searches into improving sampling and modeling techniques all pointed to the necessity of a power analysis (PA). A PA is a way of probing how systems respond to changes in variables, in this case what variables had the largest impact on the predictive power of models[118]. Variables such as number of wavelengths included, concentration, and number of samples were probed to maximize model performance while minimizing resources consumption via sample creation. The goal was determining, via a PA, if the speciation of neodymium and citrate was even sufficiently modellable with the lab technology. If successful, this power analysis would describe a methodology such that similar models could easily be generated. It would also give knowledge a priori of how many samples are needed for accurate modeling, based on known quantities such as average sample concentration (determinable by the experimenter) and amount of electronic noise in the system.

In traditional power analysis methods, the quantity of the effect size (ES) is determined via the nature of system in the analysis. The colloquial definition of ES is the extent to which the phenomenon is observable. Though vaguely described, this is the usefulness of the power analysis, because it allows for varied physical systems to be studied with the same tool, if all quantities are correctly defined. Though many more exist, the four candidates for ES are via regression, multivariate, covariance, and latent variable modeling, defined below. In regression model power analyses, the effect size is the ratio of the portion of the variance captured modeling signal (PV_s) divided by the portion of the variance capturing error (PV_E) multiplied by the ratio of the latent variables capturing signal (u) over latent variables capturing noise (v)[118]. This is congruent to the signal-to-noise ratio of the system.

$$\boldsymbol{ES} = \frac{\boldsymbol{PV_S/u}}{\boldsymbol{PV_E/v}}$$

In multivariate modeling, the ES is more involved calculation, defined below. $\boldsymbol{S}$ is the number of variables examined. $\boldsymbol{E}$ is the matrix values of the errors, while $\boldsymbol{H}$ is the matrix of the sum of squares from the hypothesis (in our case, the estimation of the correlation between absorbance and concentration)[118].

$\boldsymbol{ES} = L^{-1/S} - 1 = \frac{\sqrt[S]{|E+H|} - \sqrt[S]{E}}{\sqrt[S]{E}}$, $L = \frac{|E|}{|E+H|} = 1 - {R^2}_{Y,X}\ {R^2}_{Y,X} = 1 - \frac{|R_{YX}|}{|R_Y||R_X|}\ R_{YX} = X^T Y,\ R_X =$

$\boldsymbol{X^T X},\ \boldsymbol{R_Y = Y^T Y}$

In covariance modeling, the effect size is standard deviation of the population means over the standard deviation of the same populations. The standard deviation of the population means is the normalized difference in means of samples with equal populations to the mean of the means[118].

$$\boldsymbol{ES} = \frac{\sigma_m}{\sigma}, \sigma_m = \sqrt{\frac{\sum_{i=1}^{N}(m_i - m)^2}{N}}$$

For latent variable modeling, the effect size is the increase in R^2 from adding the latest latent variable divided by one minus the same R^2 [118].

$$\boldsymbol{ES} = \frac{\Delta R^2}{(1 - R^2)}$$

Each of these methods present their own merits for a power analysis, however, from literature, the regression model power analysis appeared the most applicable. This was partially due to a signal-to-noise ratio not only being easily observable, and also because PLS seeks to maximize signal while minimizing noise.

In a regression model power analysis, there are four key parameters, α,β, N, and ES. Type I error rate in the classical sense (the false-positive rate, or also the frequency in which the null-hypothesis is true but incorrectly rejected) is α[118]. Similarly, the type II error rate (the false-negative rate, or rate at which the null-hypothesis is incorrectly accepted) is β[118]. For ease of calculations, 'power' is used as 1- β. Explained in more detail later, the effect size for the UV/Vis models was believed to be the signal to noise ratio of the spectra. Finally, N is simply the number of samples for the system. The effect size is inversely related to α and β, as larger effects reduce both false negative and false positive rates. Further, increasing N (samples) decreases both α and β, while N has no influence on effect size and vice versa.

4.4 Speciation and Advanced Reprocessing

The last set of experiments for this thesis probed modeling speciation of complexes. Speciation is the process by which chemical reactions can generate multiple products based on the physical conditions of the reaction, such as temperature or pH. A case study of this is examined in this thesis because it is observable via UV/Vis. Specifically, the binding of a metal to a ligand changes the electronic structure of the Nd which can be observed spectroscopically[119,120]. The system studied is Nd binding with citrate in an increasing pH environment. As the pH increases, the complexing of Nd to citrate species becomes more favorable, and the composition of the solution changes with constant metal and ligand concentrations[119]. This phenomenon is of interest to study because it is a result from a separate physical entity of the metal itself, therefore monitoring process conditions via pH gives another layer of security for safeguarding. The neodymium-citrate system is of interest due to its relevance to advanced nuclear fuel recycling[36]. In advanced fuel recycling, the objective is not just to re-appropriate the uranium (and potentially

the plutonium) for reactor fuel, but also separate out specific actinides to lower the longevity of the nuclear waste. Recycling waste lowers the radioactivity by an order of magnitude much earlier in the waste lifetime. Though the end total radioactivity is not much less, it becomes safer sooner, alleviating the need for as robust long-lived safeguarding. By performing advanced fuel recycling, to transmute minor actinides americium and curium in the nuclear fuel, the fuel reaches the steady state radioactivity of the normal waste in five orders of magnitude less. Furthermore, the waste reaches a substantially lower radioactivity level, one that requires minimal safeguarding (below the natural uranium point, the toxicity of the chemicals will be more of a threat than the radioactivity). The final work of this thesis is to study the speciation via UV/Vis and model the species formation with pH changes in the ALSEP process.

Chapter 5: Materials and Methods

5.1 Sample Preparation and Validation

Metal samples were made by first dissolving neodymium nitrate ($NdNO_3$), holmium nitrate ($HoNO_3$), and samarium nitrate ($SmNO_3$) in aqueous 1M nitric acid (HNO_3). This created stock solutions which were validated via inductively coupled plasma mass spectrometry (ICP-MS). The stock solutions were 0.41 M for Ho, 0.43 M for Sm, and 0.48 M Nd. Samples were made in two sets, partially represented below.

	Set 1	Set 2
Number of samples with 3 metals	12 (16.9%)	6 (9.4%)
Number of samples with 2 metals	23 (32.4%)	6 (9.4%)
Number of samples with 1 metal	36 (50.7%)	52 (81.2%)
$[Ho]_{avg}$ in 3 metals	[0.076]	[0.014]
$[Sm]_{avg}$ in 3 metals	[0.078]	[0.014]
$[Nd]_{avg}$ in 3 metals	[0.088]	[0.016]
$[Ho]_{avg}$ in 2 metals	[0.026]	[0.021]
$[Sm]_{avg}$ in 2 metals	[0.027]	[0.021]
$[Nd]_{avg}$ in 2 metals	[0.031]	[0.024]
$[Ho]_{avg}$ in 1 metal	[0.060]	[0.073]
$[Sm]_{avg}$ in 1 metal	[0.062]	[0.088]
$[Nd]_{avg}$ in 1 metal	[0.070]	[0.081]
Overall $[Ho]_{avg}$	[0.052]	[0.053]
Overall $[Sm]_{avg}$	[0.053]	[0.059]
Overall $[Nd]_{avg}$	[0.061]	[0.060]
[Ho] Range	[0.004] – [0.206]	[0.001] – [0.412]
[Sm] Range	[0.004] - [0.213]	[0.002] – [0.426]
[Nd] Range	[0.004] - [0.240]	[0.001] – [0.480]

Table 5.1 Statistics of Pure Metal Model Sample Sets.

The objective of Set 1 was to test the interaction between multiple metals. It was of interest to study if PLS regression could correctly model sample concentration with samples containing more than one metal, or if the superposition of spectra would introduce larger errors. For this reason, nearly half of the samples contained more than one metal. For the second set, it was of interest to see the accuracy of model interpolation versus extrapolation, thus a wider set of concentration samples were generated. This was to allow for greater freedom in model

concentration ranges. This second set also allowed for a greater variability in average sample concentration while keeping sample concentration maximum and minimum constant.

For the speciation experiment, potassium hydroxide stock was created by dissolving solid KOH pellets in micropure water. The stock solution of KOH was pH validated via a potentiometric auto-titrator. The KOH was utilized to pH adjust Neodymium-Citrate samples. A stock solution of citric acid was created by dissolving solid anhydrous citric acid granules ($C_6H_8O_7$). This citric acid would then be contacted with dissolved neodymium, and then pH adjusted via the KOH stock. There were multiple batch samples, ranging from a 0.25:1 to a 4:1 ratio of neodymium to citrate. The Nd-Citrate was pH adjusted with a large range of KOH concentration adjustments, to provide for a rich pH profile. The first batch contained samples of varying neodymium and citrate ratios, and had KOH continually added to shift pH to above 7. The second batch had a constant ratio of 4:1 citrate to neodymium in a 0.5 mL volume, and samples were contacted with 0.05 mL KOH in varying concentrations shown in Figure 5.1. Resultant samples ranged from pH of 1 to 7.

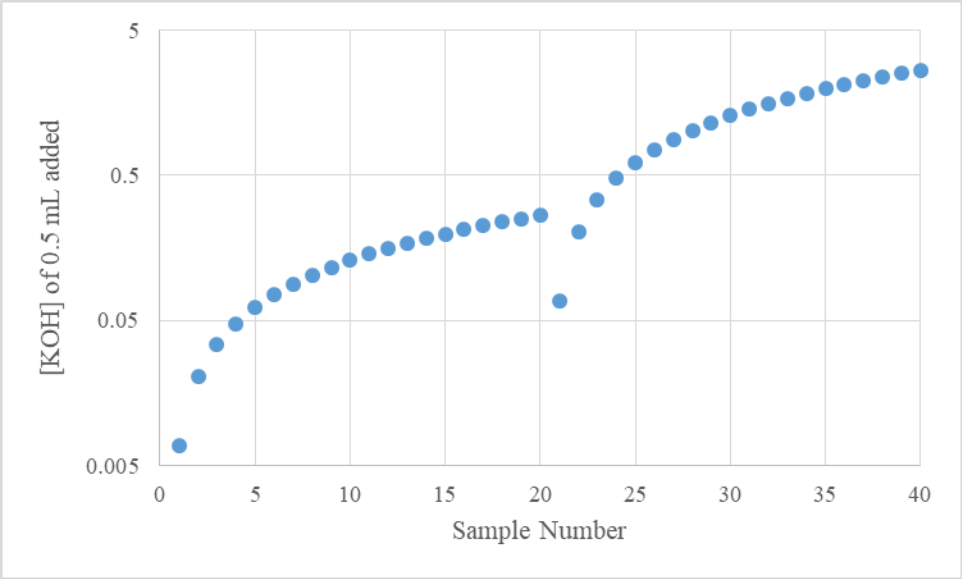


Figure 5.1 Varying Concentration of KOH utilized in 0.5 mL quantities for pH adjustment.

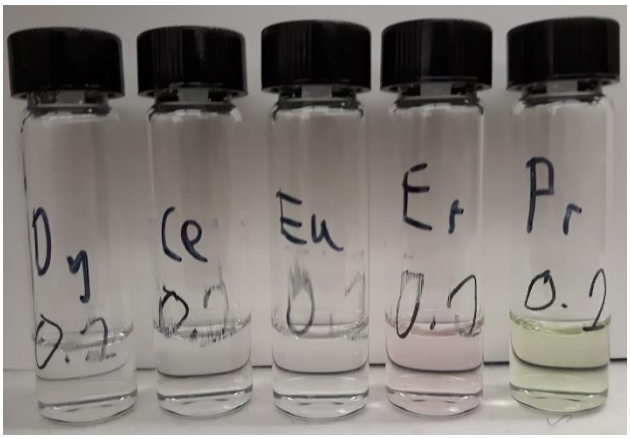


Figure 5.2. Stocks Made of Dysprosium, Cerium, Europium, Erbium, and Praeseodymium for False-Positive Testing.

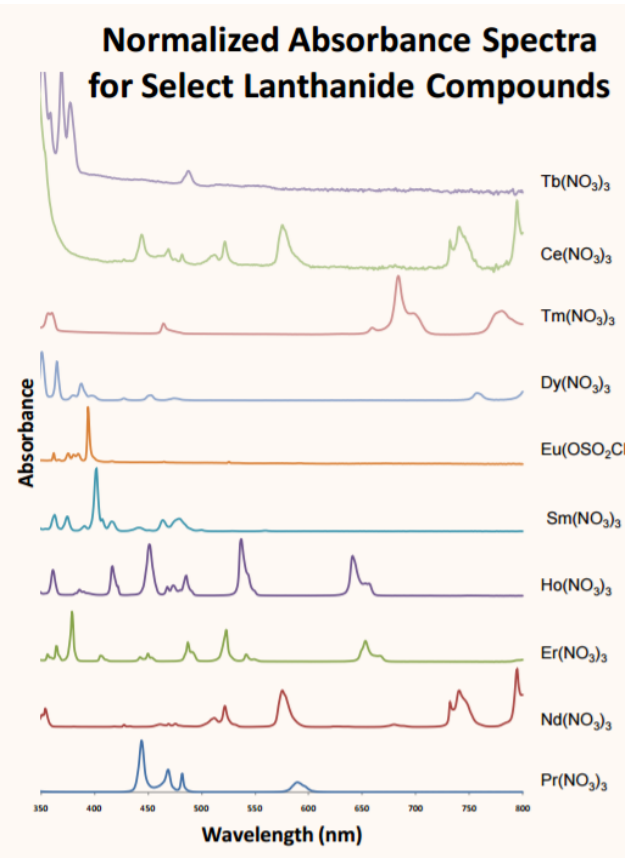


Figure 5.3. Normalized Absorbance Spectra for Nitrate Lanthanide Species. Provided from Burghard, *et al.*[121]

Samples of Dysprosium, Cerium, Europium, Erbium, and Praseodymium were created by dissolving their nitrate complexes in nitric acid to produce roughly 1 M solutions shown above. These metals were chosen due to their spectral overlap with target metals Ho, Sm, and Nd. Specifically, Erbium, Praseodymium, and Dysprosium were to mimic Holmium; Europium and Dysprosium were to mimic Samarium; and Cerium, Erbium, and Dysprosium were to mimic Neodymium.

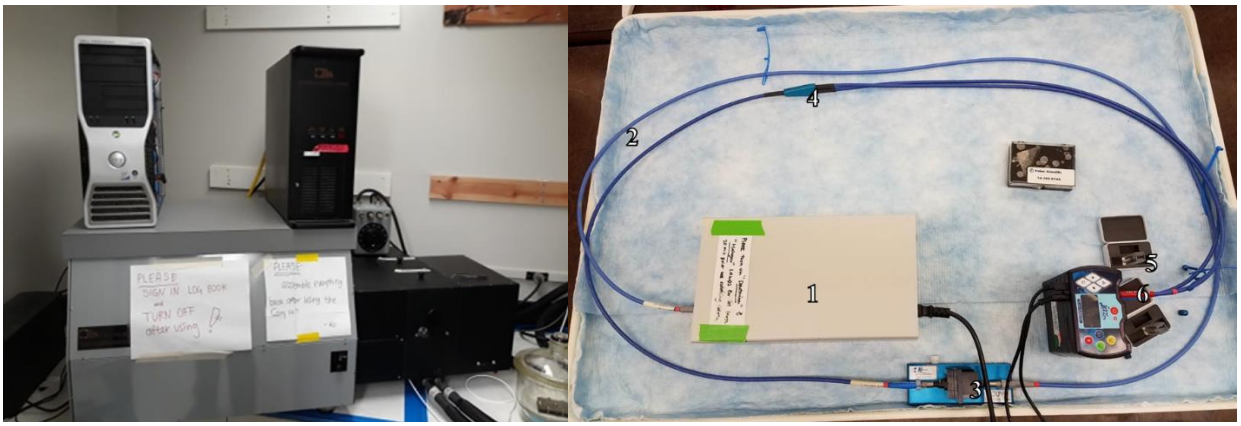


Figure 5.4. Cary-14 and Jaz Spectrometer used for Absorption Measurements.

Absorption measurements were taken by the set up shown in Figure 5.4. An OceanOptics Mikropack Deuterium/Halogen light source (1) generated light between wavelengths 230 to 2500 nm, which transversed an OceanOptics short range fiber optics cable with a 400 µm diameter and a 2m length (2). The light traveled into a cuvette holder and dark chamber (3). In the cuvette holder was a Suprasil® quartz cuvettes (5) with a 1 cm pathlength and 200-2500 nm spectral range. The light then passed into an OceanOptics UV/Vis/NIR bifurcated cable (4) with a 400 µm diameter and 2m length. The light then was measured via an OceanOptics Jaz-Spectrometer (6). Channel 0 covers wavelengths from 200 to 900 nm while channel 1 covers 500 to 1200 nm. The integration time of the spectrometer was set to approximately 7 milliseconds for the first channel and 8 for the second. Lowering the integration time prevented the light intensity from maxing the signal to the detector, which would prevent calibration as the true value of the output of intensity would not be known. As shown below, each lamp had a characteristic intensity curve.

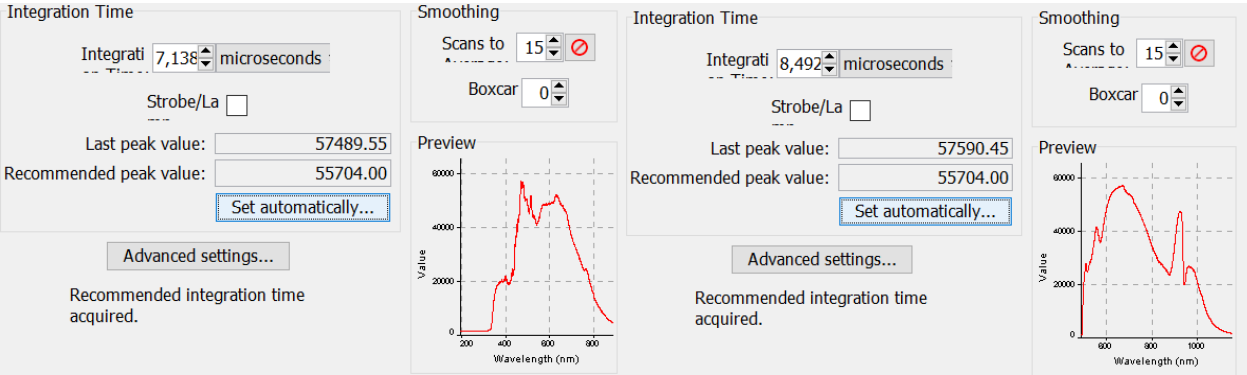


Figure 5.5 Integration Times to Observe Full Intensity Spectra of Both Spectrometer Channels.

Once appropriate integration times were determined, spectra were recorded in the two channels. Channel two gave data from 200 to 890 nm, however nitric acid interference heavily skews the absorbance and thus was removed from 200 to 345 nm during preprocessing.

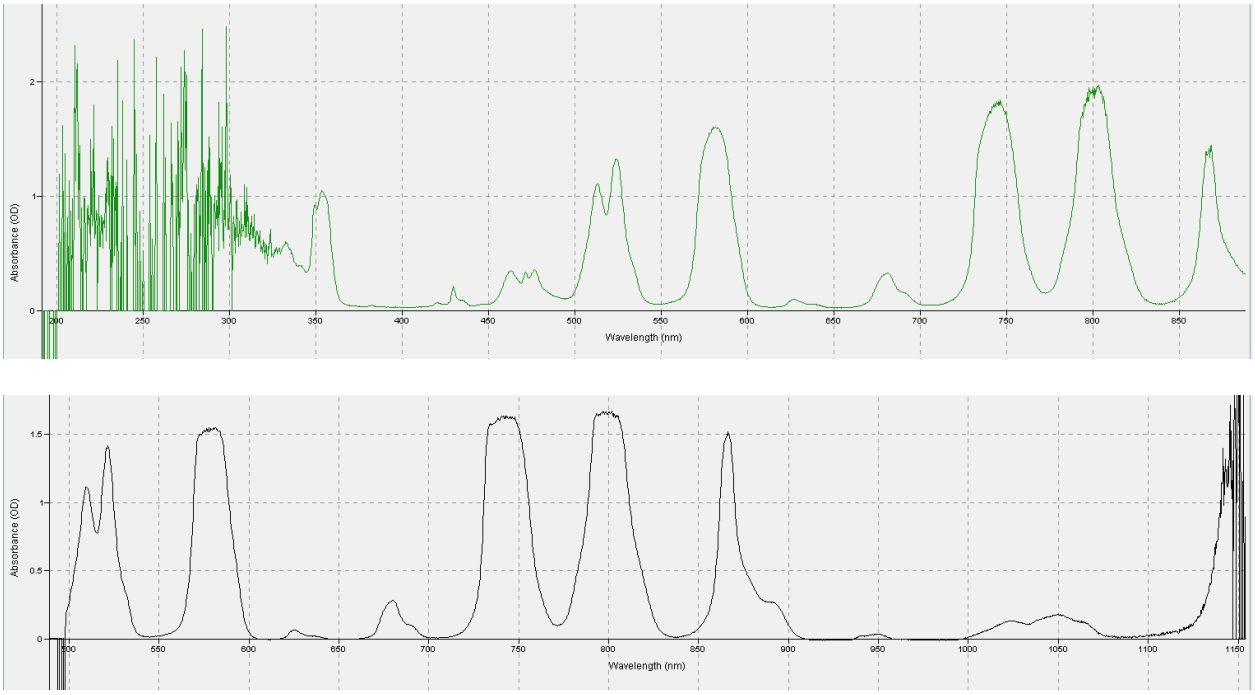


Figure 5.6. Absorption Spectra of Neodymium in Both Channel 1 and 2.

The second channel recorded absorbance from 480 nm to 1200 nm, however, due to edge effects of the spectrometer's limit, data was only kept from 500 to 1060 nm. The Cary-14 Spectrometer (with an operational range of 200-2600 nm and pictured left) was utilized to gather additional sets of spectra.

ICP-MS operates by ionizing samples via plasma field created by varying magnetic field (specifically creating an electric field via electromagnetic induction). Samples are then separated based on a charge-to-mass ratio and creates a signal relative to concentration which is sent to the mass spectrometer. Concentration is then determined via calibration of a reference, in this case Indium (In).

5.2 Data Collection

After spectra were generated, a baseline correction was necessary due to an unnoticed drift in several samples. Displayed below is two near-identical spectra showing a change in absorbance above what is the 'normal' spectra, showing a flat baseline in Figure 5.7 (left). Unfortunately, the shift was observed only after several samples were collected with it present and was not handled before-hand. As re-collecting the blank sample and regenerating the spectra removed it, it was believed the source of error was electronic noise. However, some samples had already been disposed before this was caught. Because the shift was small, nearly-linear, and uniform, it was decided to perform a baseline correction on the spectra rather than recreating samples. The correction was performed by selecting points of non-zero absorbance in the spectra where previous research shows zero absorbance. These points where fit using least-squares to create a

polynomial to describe the shift. This polynomial was then subtracted from the base-shifted spectra, creating spectra with better agreement of previous research. The result is plotted below.

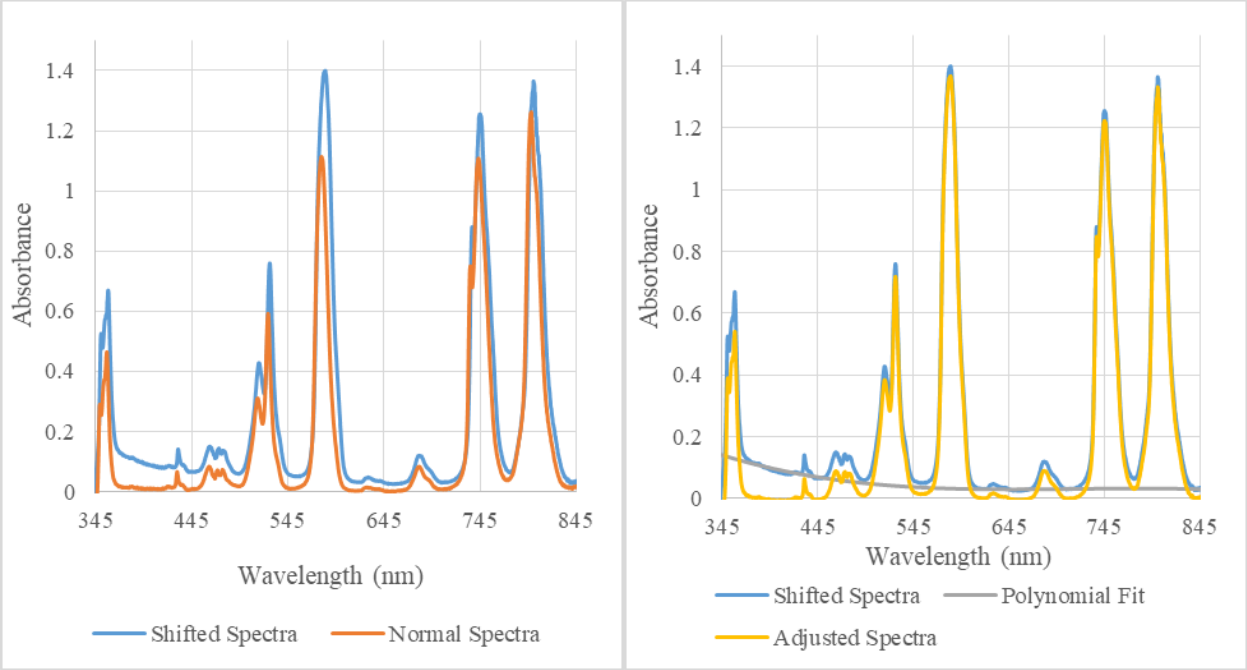


Figure 5.7. Comparison of Spectra Before (left) and After (right) Baseline Corrections for Drift.

5.3 PLS Modeling

For PLS modeling, the data was cross-validated via contiguous blocks method. The preprocessing was set to autoscaling. This created the best results, as measured by RMSEC, RMSECV, and RMSEP. After models were created, the number of LV's was selected. Latent variables were selected to capture the first and second order of magnitude of variance in both X and Y blocks. This was generally 5 LV's, though some had 3 or 4. More LV's generally introduced more noise than they captured variance. The exception was comparing models where it was desired to keep the number of LV's constant.

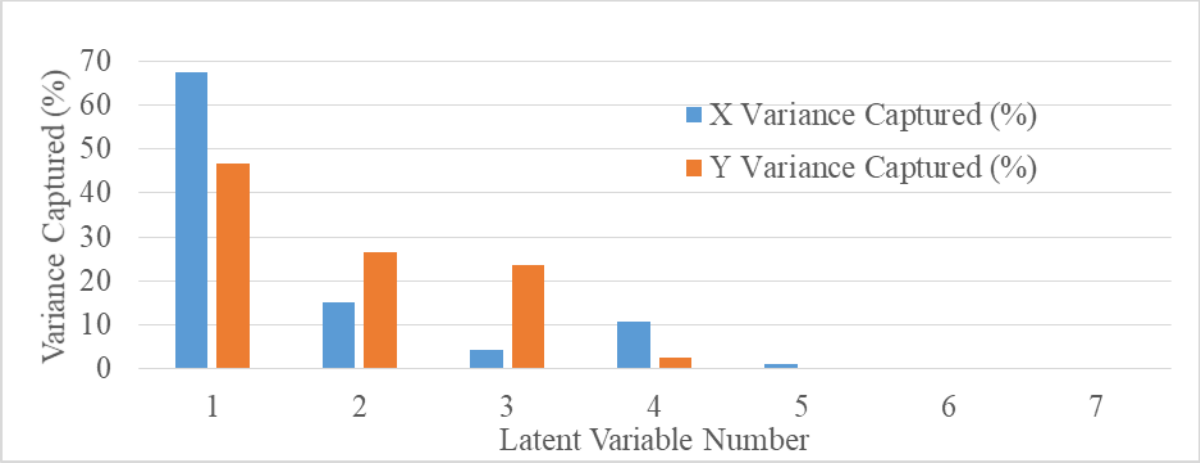


Figure 5.8. Variance Captured Per Latent Variables from both X and Y Blocks.

In traditional PCA and some regression methods, LV's are created to have monotonically decreasing X variance. However, in PLS the desired output is maximized X and Y variance, thus the LV's are organized so the sum total of variance of both blocks is maximized. For example, LV 3 and LV 4 would be switched in other methods, as LV 4 has more X variance than LV 3, but since the net variance (X plus Y) is higher, LV 3 comes first.

CHAPTER 6: Meta-Analysis of Multi-Metal Modeling

Eventually a literature search on PLS modeling lead to the idea of conducting a power analysis on the system of interest[122]. The goal of the power analysis was to elucidate quantities that influenced modeling accuracy. As described in greater detail above, a power analysis is a heuristic to relate describable qualities of the system to type I and II errors. Specifically, the quantities of interest here are α, P, N, and ES. By completing a power analysis, it would allow modelers to know a priori how accurate their models could be based on the absorptivity of the materials of interest and the given spectrometer. This would allow similar systems to know how well safeguards would work without needing large volumes of material for samples.

6.1 Power Analysis Quantity Calculation

A preliminary study showed correlation between increasing concentration and decreasing the RMSEP. Unfortunately, the initial study was conducted on large N (50) models. This created a problem in that creating models with smaller average concentration would influence other variables that initially were believed could affect RMSEP, and thus potentially conflate variables. These variables included minimum sample concentration, maximum sample concentration, and total sample number. Based on the literature review described in chapter 4 of this thesis, it was determined that sample number would be investigated with signal-to-noise ratio of the UV/Vis spectra. The signal to noise ratio was defined as the absorbance of the spectra due to sample metal concentration divided by the absorbance fluctuations due to electronic noise. The process was the absorbance of pure metal samples were divided by their corresponding metal concentrations, creating approximate attenuation coefficients which were then averaged

over the samples of the same metals. This created a vector of molar attenuation coefficients. Then, the original absorbance of each sample subtracted the concentration of the other two metals multiplied by their coefficients. The product was the absorbance only due to the one target metal. The noise was calculated similarly, except all metals were subtracted out, leaving only random fluctuations. The standard deviation of blanks would also qualify as the noise of the system, and in fact was used to compare methods (standard deviation of blanks yielded an average absorbance of $\pm$0.0018, while the more involved method was $\pm$0.0026). The logic arguing for using a more involved calculation of noise was it was the most similar in calculation to signal. The explicit equation is below.

$$SNR = \left. A_n - \left[\frac{\sum_{n=1}^{N} \frac{A_n}{C_{n,i}}}{N} * C_{n,i} \right]_{j,k} \right/ A_n - \left[\frac{\sum_{n=1}^{N} \frac{A_n}{C_{n,i}}}{N} * C_{n,i} \right]_{j,k,l}$$

6.2 Effect of Sample Number

After a formulation of SNR, sets of models were made with constant maximum, minimum, and average concentration. The results are plotted below. Larger N model sets had smaller variance, likely due to larger N models having more overlap in the specific samples included as compared to smaller N sets, which could have completely unique samples. The independence of SNR to N was expected; as SNR was the hypothetical ES, it should not change with N as theory predicts. However, RMSEP did not vary noticeably with N, which was not expected. As RMSEP is a measure of both type I and II errors, and errors should decrease with increasing N, it was expected RMSEP would decrease slightly with higher N. There is a stark increase in SNR at very

low sample number (3 & 6 N models) for Neodymium and a less noticeable effect for Holmium. However, due to the very low sample number, and the fact the SNR is calculated via averaging, the calculation is overinflating the signal and not able to correctly describe the noise of the system.

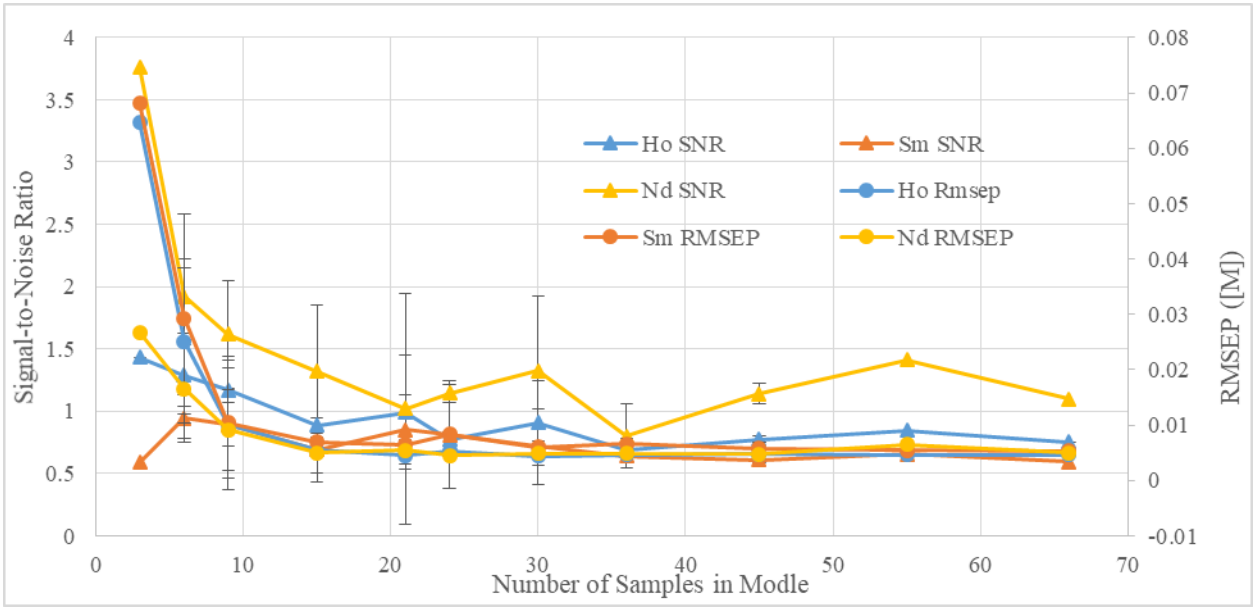


Figure 6.1. Relation between Signal to Noise Ratio and Sample Number Showing No Improvement with Additional Samples.

6.3 Effect of Signal-to-Noise-Ratio

Generation of these model sets allowed further inspection of the influence of concentration to RMSEP. This showed an unexpected result of the ineffective nature of average sample concentration on RMSEP. The previous exploratory investigation was using samples with average concentration between 0.04-0.07 M metal, which appeared to have an influence on modeling performance. However, when models could be made at much lower sample concentration with the same or lower errors, this disproves the hypothesis of a correlation.

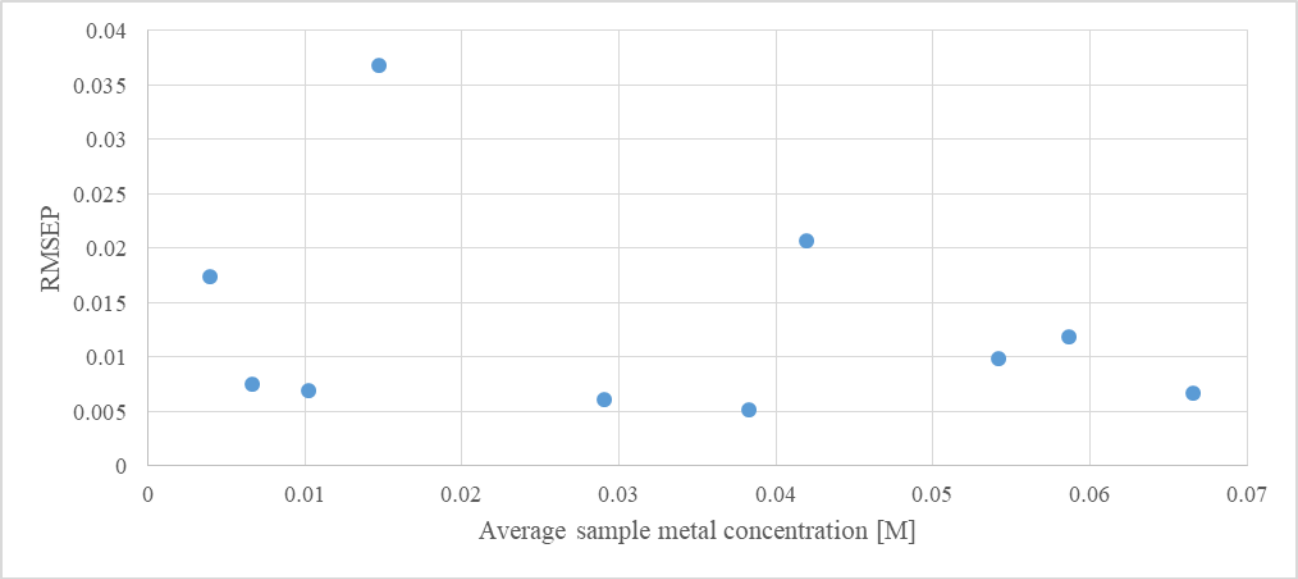


Figure 6.2. Average Concentration of Samples utilized in Modeling Does Not Increase Predictive Power.

The power analysis was unfortunately not successful in elucidating methods for improving modeling and sampling techniques. It did, however, reveal that large N models are not necessary, and accurate models can be made with as low as 20 samples. The best option for future work for relating key variables to predictive power would be combination of variables (conducted via PCA or copulas) which may have a more observable and pronounced effect. Through the speculation of how to improve modeling accuracy though, our research turned to the idea of exploring the effect of number of wavelengths included in a model. The next chapter explores this concept in full.

6.4 Effect of Max Concentration

After confirming no relation between the average sample concentration of metals and the predictive power of the models, we briefly explored the effect of the maximum concentration

present in the model and predictive power. Though the previous two studies did not hint the effect would be substantial, the data was readily available and easily modelled. Models were made with samples having a max concentration between 0.02 M and 0.5 M, utilizing models of Holmium, Samarium, and Neodymium. There was not a strong relation between max concentrations of samples as seen in Figure 6.3. At the tail end (roughly below 0.05 M max concentration) though it appears at the tail end there is a stark incline. This is due to the sample number approaching the point that sample number starts to have an effect and overfitting is occurring in the model (around M = 0.035). The region of 0.04-0.5 M has effectively no slope between the two quantities of interest while decreasing linearly with sample number. When comparing Figure 6.3 and Figure 6.1, the shift in RMSEP in the region below 0.04 M max concentration is congruent with the overfitting shown in Figure 6.1. Though not ideal to vary RMSEP with both max concentration and sample number, as the dependency of RMSEP on sample number was already elucidated, so the effect of sample concentration could be derived.

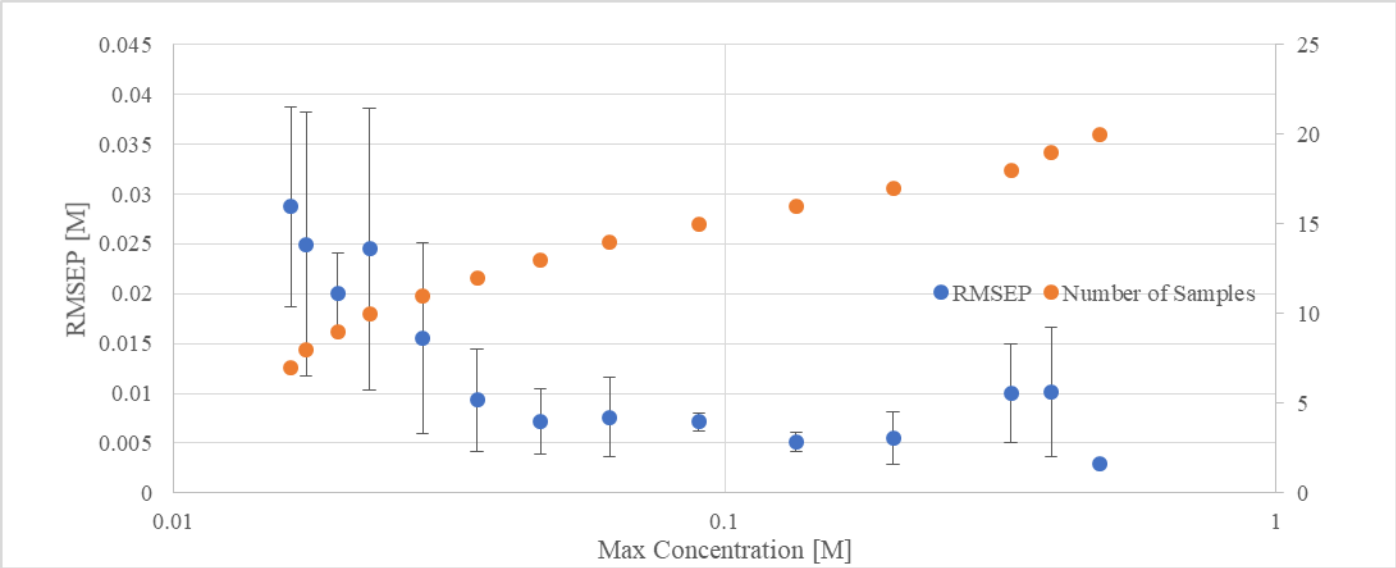


Figure 6.3. Increasing the Max Concentration Does Not Improve Model Predictive Power Until Sample Number Becomes Too Low.

6.5 Detector Comparison

The final meta-analysis of the models generated in this work was testing the discrepancies between samples recorded across different detectors. The samples were generated and verified with a model calibrated via ICP-MS. The same samples were then analyzed on the Carry-14 spectrometer. The output is shown below. On the lower samples, there is almost perfect overlap between spectra. However, at higher samples, there is noticeable discrepancy, along with the Cary-14 recording maxed absorbance for several peaks. This inflate errors drastically, so these regions of the spectra were removed before modeling.

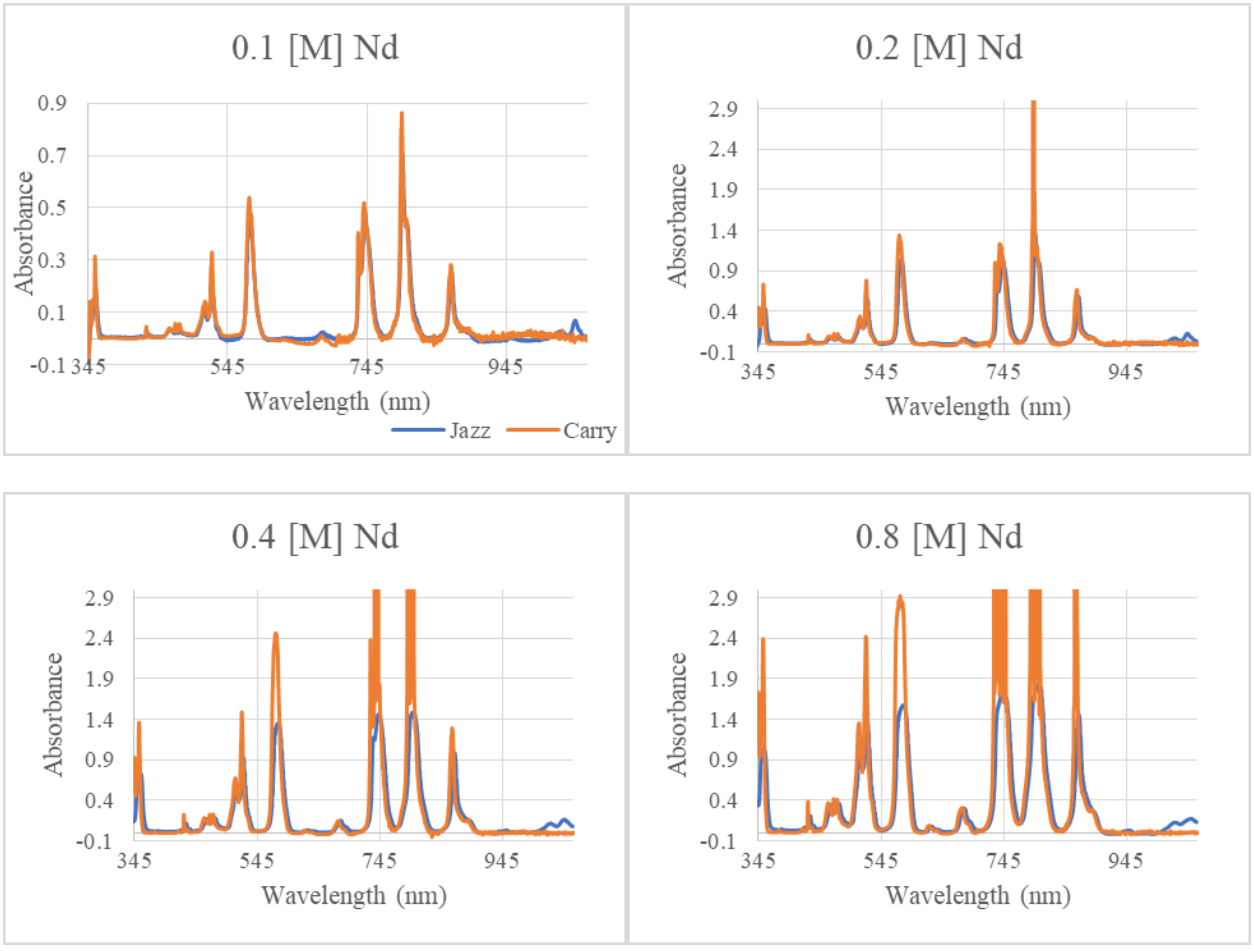


Figure 6.4. Comparison of Absorbance of Neodymium at Four Concentrations Recorded on both Jaz and Carry-14 Spectrometers.

The model indicated a slight discrepancy at lower values (0.07-0.4 M) while the largest error was in the 0.74 M Nd sample. The overall model discrepancy was an %RMSEP of 15% between the two detectors. However, without the last concentration set, the %RMSEP drops to below 5%.

Modeling Results between Spectrometers		
	Measured Concentration	Predicted Concentration
0.1 M Nd	0.0794	0.0763
0.2 M Nd	0.2032	0.1912
0.4 M Nd	0.3983	0.4127
0.8 M Nd	0.7419	0.8495
RMSEP	0.0546	
%RMSEP	15.3610	

Table 6.1. Modeling Results Showing 15% Error in Average Prediction in Models.

CHAPTER 7: Wavelength Selection and Inclusion for Robust Modeling

In the previous chapter, we examined the potential to estimate model efficacy based on minimal knowledge, to simultaneously save material and time while elucidating key modeling parameters. Unfortunately, tests were inconclusive on experiments to relate logical candidates (sample number, and signal to noise ratio) to desired outputs (%RMSEP). However, in our literature search and trials, we became interested in the effect of expanding spectra examined beyond peaks. Traditionally in chemometrics and UV/Vis spectra modeling, variable selection is a key component where only the peaks most sensitive to changes in the environment are utilized[123,124]. This is to minimize noise and improve accuracy. Though accuracy is still the main importance, because the model is made for special nuclear material safeguarding, robustness has a heightened emphasis. Thus, we wanted to make the model less susceptible to false positives that would misidentify material as our target metal. Our hypothesis was that by including wavelengths where our target metal does not absorb, but other metals could absorb, we could generate a model that negatively correlates target metal concentration to absorbance at this location, thus acting as a safeguard against conflating the two chemicals. However, to test the effect of including additional wavelengths to a model, we first needed to verify that specific wavelengths themselves were not more or less valuable; that mostly each wavelength contributed equal signal and noise. To accomplish this, we utilized a genetic algorithm to test the effect of including and removing specific wavelengths across the whole spectrum from our UV/Vis detector. The algorithm was prebuilt in the PLS package utilized for this research, and the output and results are detailed below.

7.1 Genetic Algorithm for Variable Selection

Two representative graphs of the genetic algorithm are shown below. The genetic algorithm was utilized to probe the effect of changing wavelengths across models. In many chemometric models, some wavelengths provide more signal than noise. However, while using three metals that have absorbance peaks at mostly the entire spectra, this was not seen to be the case. From the high (254) end to low (14) end populations, no wavelengths stood out as particularly more useful than others. This is reflected in Figure 7.1 in that there is little to no vertical variation across wavelengths used (no colors being absent in a given region of wavelength). Though some wavelengths appeared to have little utilization (around 600 nm), close inspection showed that it could be used to produce models at both high and low end accuracy. If a given segment of wavelength was contributing significant errors, there would exist models at the high end of the Y-axis (consisting mostly of red colors), but no models at the low end (consisting of more blue hues). This implies the changes in wavelengths utilized in models across generations was more so influenced by the algorithm set random rate at which variables are switched on and off (referred to as a mutation rate in the genetic algorithm) than the actual performance.

This result that largely no wavelengths in the spectra analyzed were better or worse as far as increasing model performance meant that we could randomly select wavelengths at will to observe the effect of changing the number of wavelengths utilized, and the particular wavelengths in general had little to no difference.

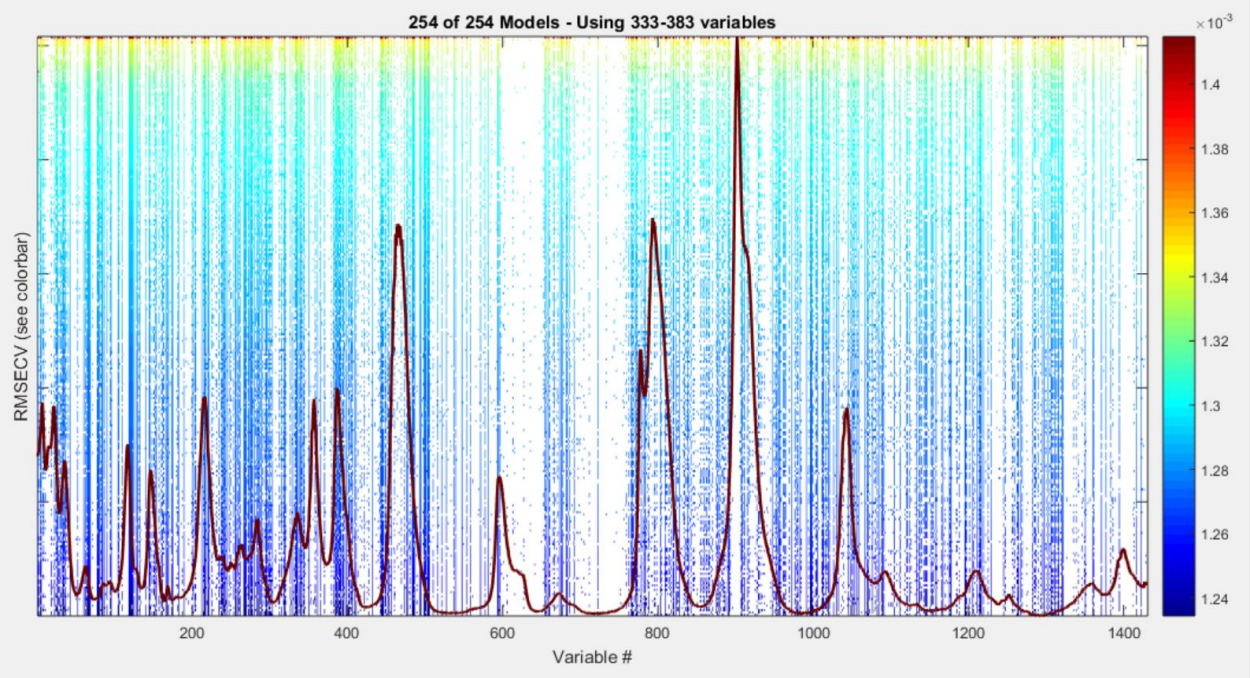


Figure 7.1. Testing Each Wavelengths' Contribution to RMSECV. Results Show Peak Selection Does Not Improve Model Performance. Effect of Wavelength on Model Performance is Indicated by Only Select Colors Being Present for a Given Variable Rather than the Entire Scale.

As mentioned previously, traditionally, UV/Vis spectroscopy utilizes peak selection to maximize signal to noise ratio. As non-absorbing regions from spectra mostly constitute noise, they can be detrimental to concentration calculations or analysis. For this reason, optimization of peaks considered is standard. However, for the purpose of special nuclear materials safeguarding, this can lead to a pitfall, as demonstrated below.

7.2 Additional Wavelength Effect on RMSEP

A model was created on a set of pure neodymium samples, utilizing only wavelengths from 518-528 nm. Though this is not the most sensitive peak in the neodymium spectra, it serves for demonstration purposes. Erbium, another lanthanide, has a very similarly absorbing peak in this

region. A test sample was examined using the pure neodymium model, and from the erbium spectra, determined the concentration of neodymium was 0.095 M. For reference, this neodymium spectra shown with close overlap was 0.068 M. This demonstrates that a model can confuse one metal for another when utilizing peak selection. For instance, when examining plutonium in nitric acid medium such as in Figure 7.2, the major peaks of plutonium are around 800 and 950 nm. As neodymium has peaks in both these regions, it could be used to trick a monitor into detecting plutonium. Generally, in processes, there will be purification steps to prevent this, but when considering the possibility of a nefarious actor, this cannot be overlooked. Including the small section of spectra from 540 to 545 nm did not have a large decrease in the accuracy of the neodymium model, as the RMSEP was 0.0052 M. However, when testing against the erbium contaminant, the new model estimated a neodymium concentration of only 0.011 M, which is an almost nine-fold reduction of concentration. This demonstrates that including additional spectral regions can improve model efficacy by reducing potential for confusion. The inclusion of additional wavelengths where the metal does not absorb at removes partial potential for a given species to be conflated with the target metal. By

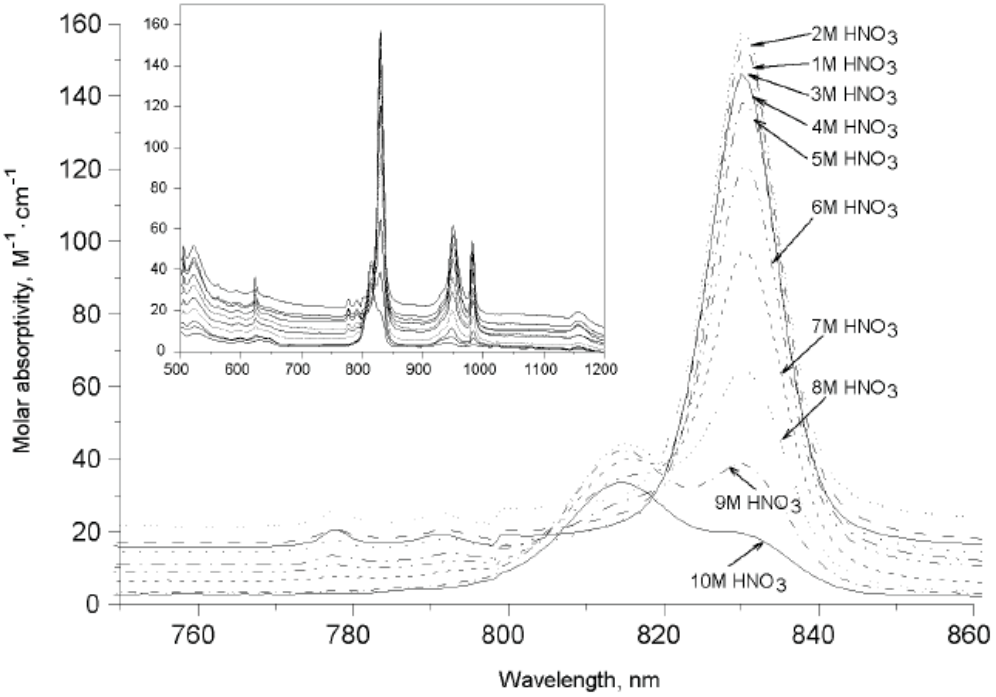


Figure 7.2. Plutonium Spectra in Nitric Acid Environment of Varying Concentrations Showing Spectral Shifts in the UV/Vis Region. Provided from Lee, Park, and Kim[125].

induction, additional wavelengths add additional robustness. The difficulty though is determining where a potential contaminant could have additional peaks. An analysis of chemicals common in spent nuclear fuel would easily reduce much of the potential unintentional contaminants, but the possibility of nefarious confusion exists. A malicious actor with insider knowledge could purposefully choose a set of contaminants to mimic uranium or plutonium in the UV/Vis region that are not commonly found in spent nuclear fuel.

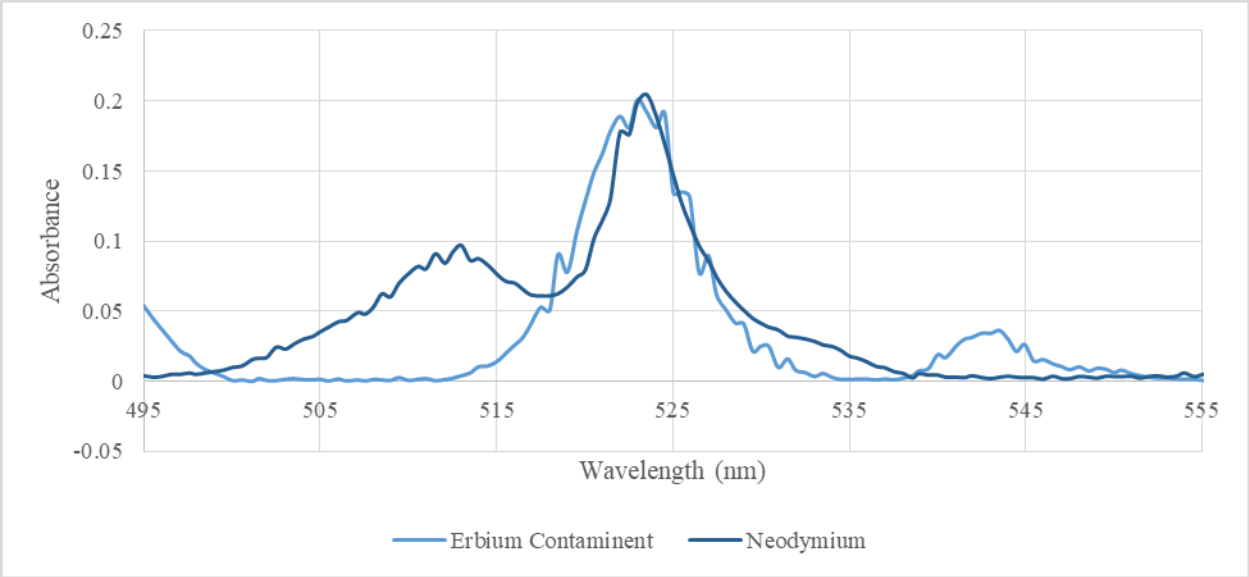


Figure 7.3. Neodymium and Erbium Have Overlapping Peaks at 515-530 nm, Allowing for False-Positives.

The following two graphs show a worst-case scenario for additional wavelengths included in a modeling set. Neodymium was utilized as a surrogate for contaminants to train the model as on absorbing peaks that are not the target metal, Holmium. In the worst case scenario, regions were chosen where neodymium absorbed, but none of the contaminants (Er, Eu, Pr, Dy, and Ce) did. This would simulate a scenario where a nefarious actor could pick contaminant(s) that absorbed where the target metal, Holmium, did, but at none of the locations the surrogate did.

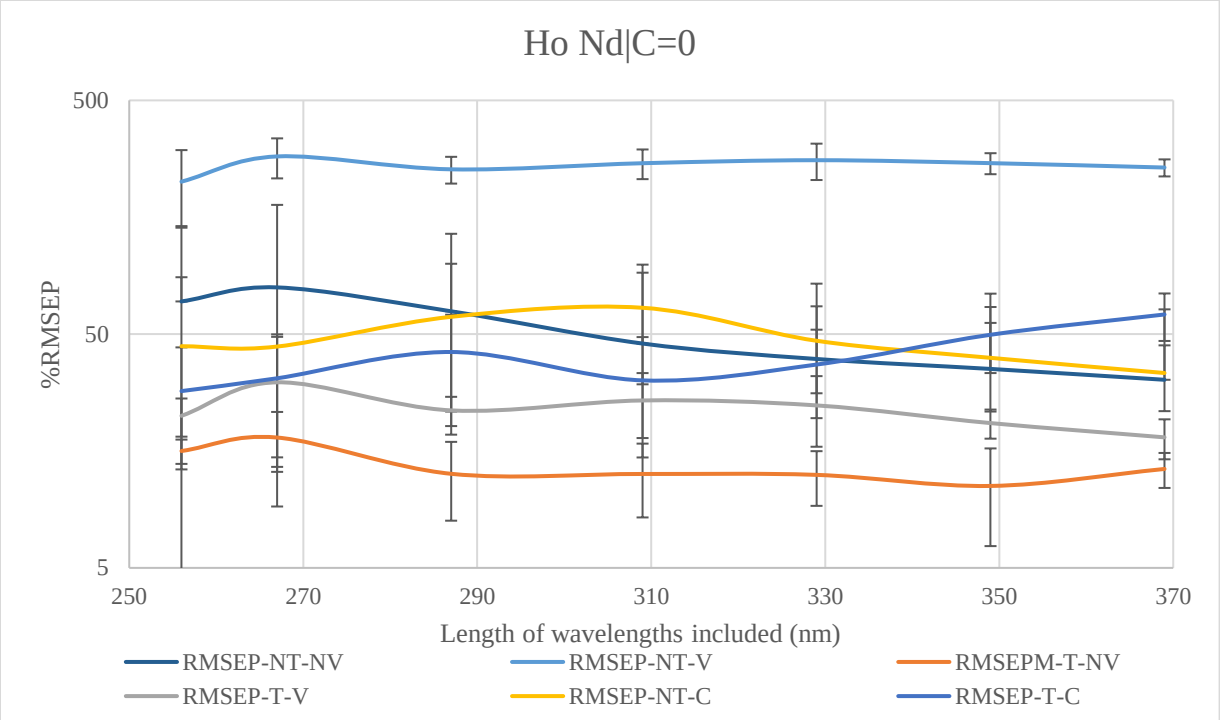


Figure 7.4. Models Made with Holmium as the Target Metal, and Neodymium Used as Surrogate to Reduce False Positives. Wavelengths were Included Where Neodymium Absorbed and No Contaminants Did.

In the above graph, there are six important quantities. The ‘NT’ tag represents Neodymium not included in the training set, while T has it present. Similarly, ‘NV’ is the surrogate not present in the validation set, while neodymium is present in the validation sets labeled V. The importance of including the surrogate in the validation set is to verify that the presence of the surrogatew would not influence the ability track the target metal. The sets labeled C have a validation set composed of solely contaminants (representing a diversion of material). The y-axis is a measure of %RMSEP, not raw RMSEP. This is the RMSEP divided by the average concentration of the target in the test set (Holmium) to make models comparable across different concentration sets. Additionally, using %RMSEP made the results more comparable because change in performance was the metric of interest, not just the raw value. For the containment set, which does not contain holmium, the average concentration was the concentration values that would lead to the same absorbance as the containments utilized. The x-axis does not correspond to the specific

wavelengths used, but rather the length of spectra, in nm, used. Thus 370 nm implies there were 370 nm total of wavelength used. The entire length was broken into segments from 345 to 1100 nm. The specific wavelengths utilized varied across three test sets to normalize for performance of certain wavelengths over others, though a genetic algorithm already implies the effect difference would be marginal.

Abbreviation	Meaning
NT	'Not in Training' – Nd Surrogate Not Utilized in Training Set.
T	'in Training' – Nd Surrogate Utilized in Training Set.
NV	'Not in Validation' – Nd Surrogate Not Utilized in Validation Set.
V	'in Validation' – Nd Surrogate Utilized in Validation Set.
Nd|C=1	All Additional Wavelengths Included Are at Wavelengths Which Both Surrogate (Nd) and Contaminants (Er, Eu, Pr, Dy, or Ce) Absorb.
Nd|C=0	All Additional Wavelengths Included Are at Wavelengths Which Only Surrogate (Nd) and No Contaminants (Er, Eu, Pr, Dy, or Ce) Absorb.
C	'Contaminent Set' – Model Tested Against Set of Contaminents with Neither Target (Ho or Sm) or Surrogate (Nd).
Ho/Sm	Results for Holmium Target with Model for both Holmium and Samarium
Ho/**Sm**	Results for Samarium Target with Model for both Holmium and Samarium

Table 7.1 List of Tags Describing Experiments in Chapter 7. Example: For graph labeled Ho Nd|C=0 and data set labeled RMSEP-NT-NV, this is the RMSEP of a model where the surrogate was not used in the training set (NT) nor in the validation set (NV) and additional wavelengths included were where the surrogate absorbed but the contaminent did not (Nd|C=0).

The importance of comparing the two cases for the training set is to elucidate that inclusion of the surrogate does not reduce model performance when only the target exists, as this scenario will the most probable encounter for the model.

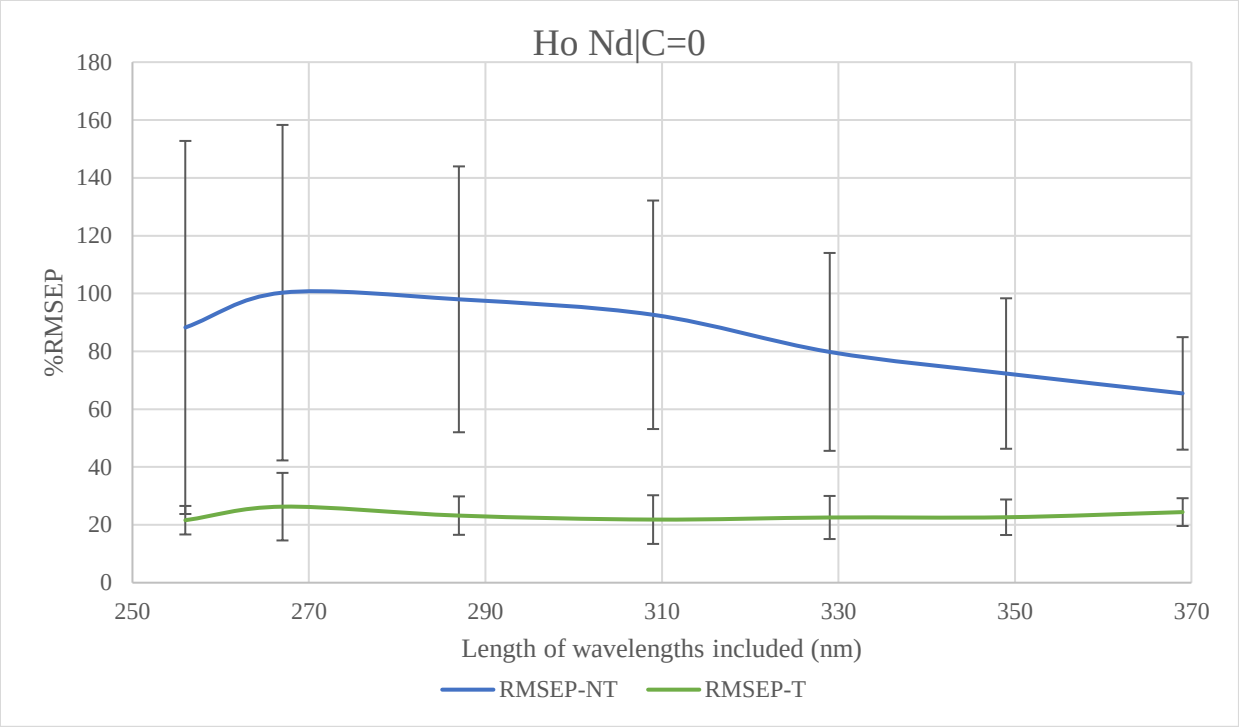


Figure 7.5. Aggregate of Model Performance Based on Not Including a Surrogate in Training Set vs. Including in Training Set. Overall, the Performance Did Not Decrease While Utilizing Additional Wavelengths.

The above graph contains geometric means of the three validation sets (‘V’,’NV’, and ‘C’) compared as performance of including the surrogate in the training set vs. not including. The importance is to show that overall, model performance does not worsen when including more wavelengths when the training set included the surrogate. This suggests that additional wavelengths can be included into a modeling set that do not contain absorbance peaks of the target without worsening performance. The additional wavelengths included could potentially be at locations contaminants could have absorbing peaks. Though there is no significant decrease in error, there is an implicit accuracy gained in that a species absorbing at target metal peaks but also at additional peaks could be discriminated against.

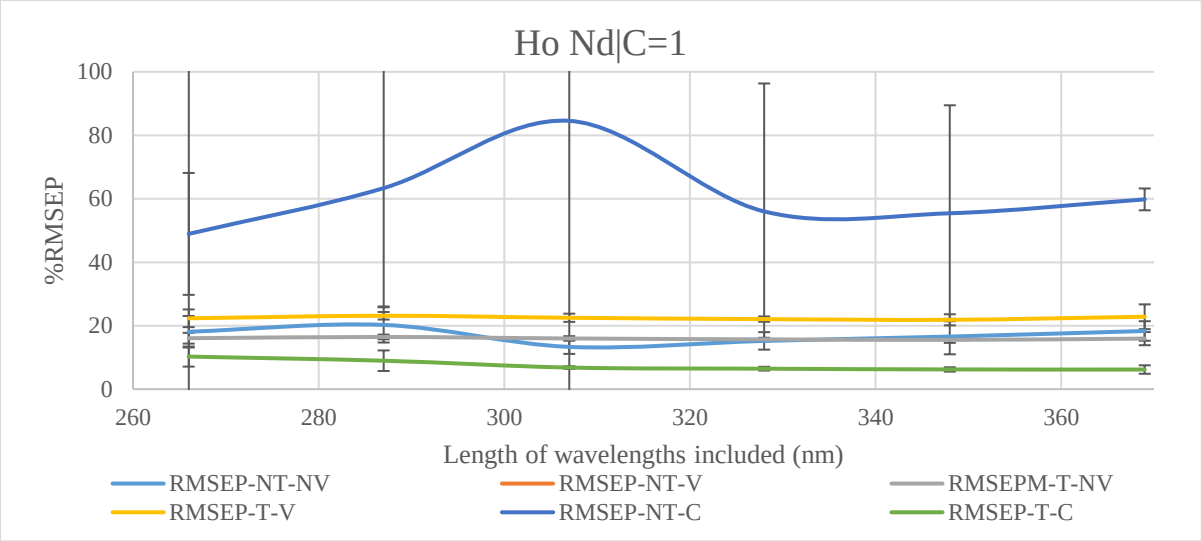


Figure 7.6. Models Made with Holmium as the Target Metal, and Neodymium Used as Surrogate to Reduce False Positives. Wavelengths were Included Where Both Neodymium and Contaminants Absorbed.

The above graph was a simulation of the best case scenario for the surrogate. Specifically, every additional wavelength included was at a wavelength where both the surrogate and contaminant absorbed. In this test, the trend argues more strongly for including additional wavelengths. Again, the set where the surrogate was included in the validation but not the test set was a much higher error.

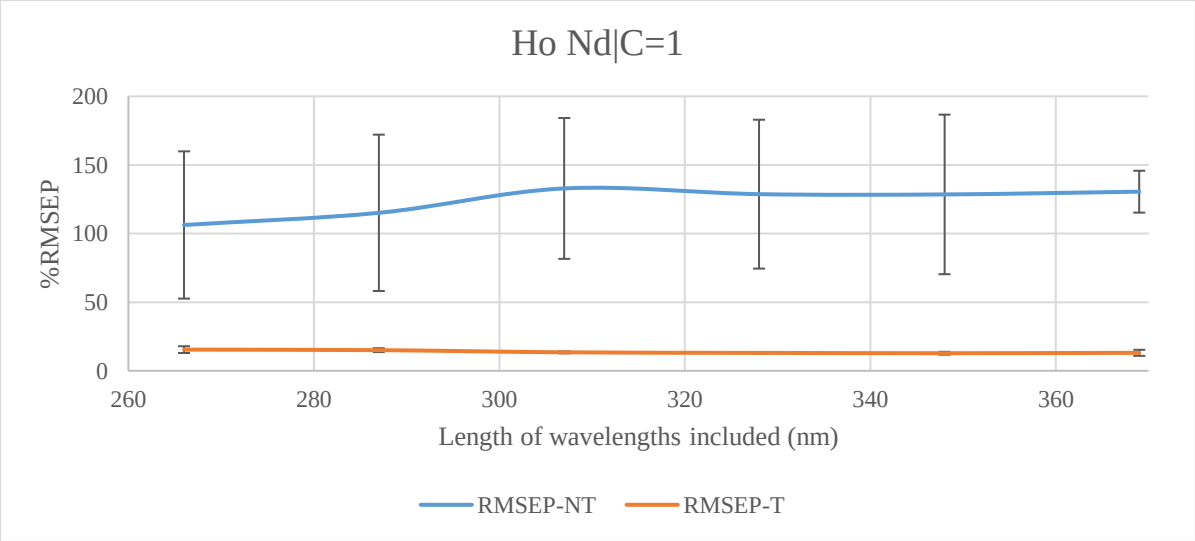


Figure 7.7. Aggregate of Model Performance Based on Not Including a Surrogate in Training Set vs. Including in Training Set. Overall, Performance Was Constant While Utilizing Additional Wavelengths.

In the case of including only additional wavelengths where both the surrogate and contaminant absorbed, including additional wavelengths did not affect the performance when the surrogate was included in the training set. This suggests there is no setback to including surrogates, while the argument for inclusion is reducing potential for model confusion.

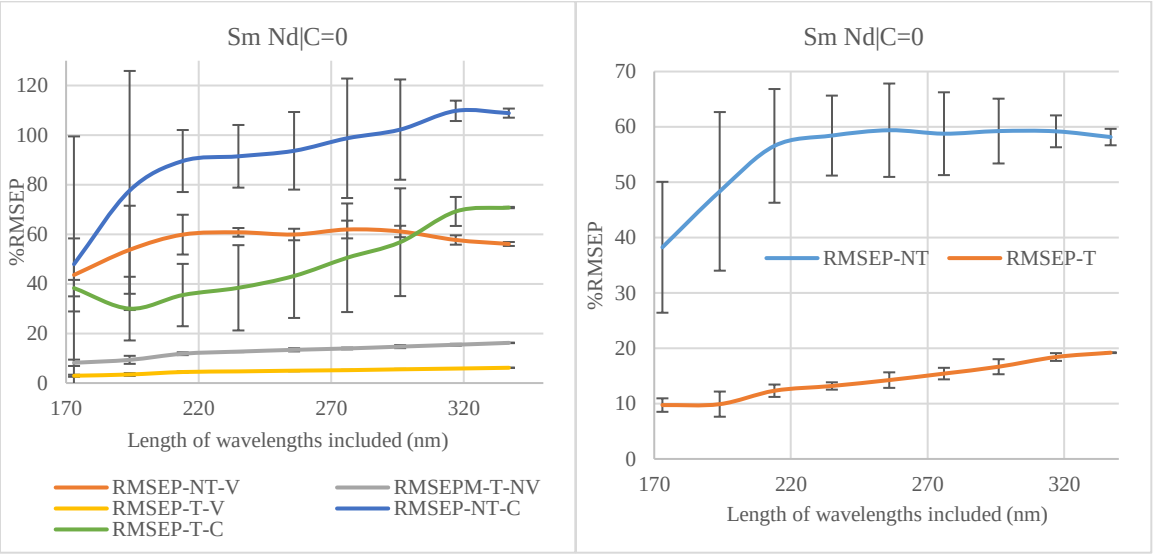


Figure 7.8. Holmium and Samarium Models with Samarium Results. Including a Surrogate in the Training Set Improved Model Performance Compared to No Surrogate Despite the Additional Wavelengths Included Not Overlapping with Contaminant Absorbance Peaks.

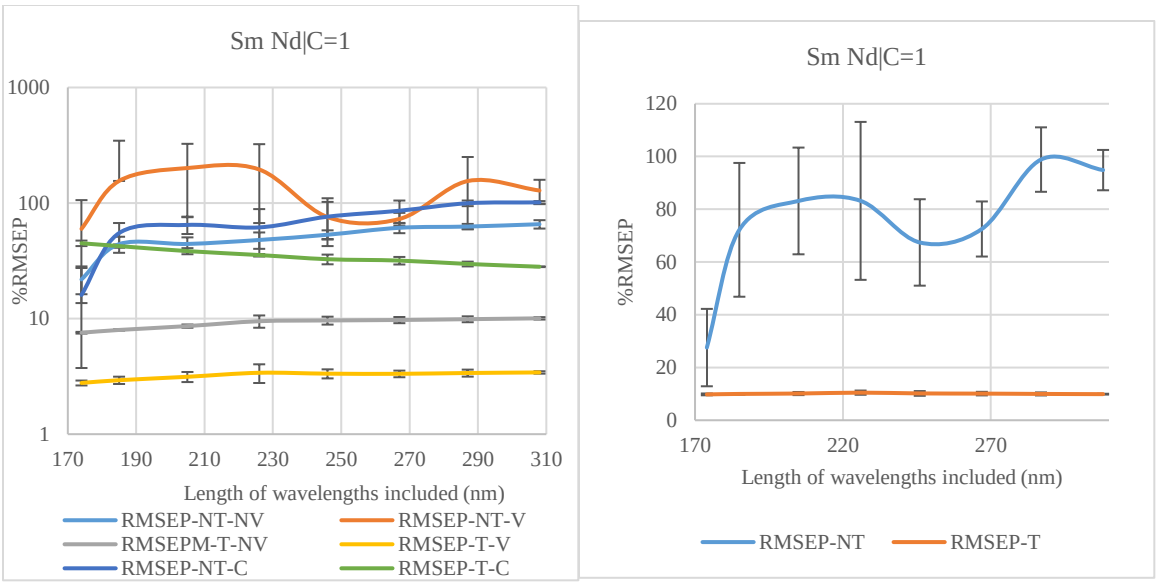
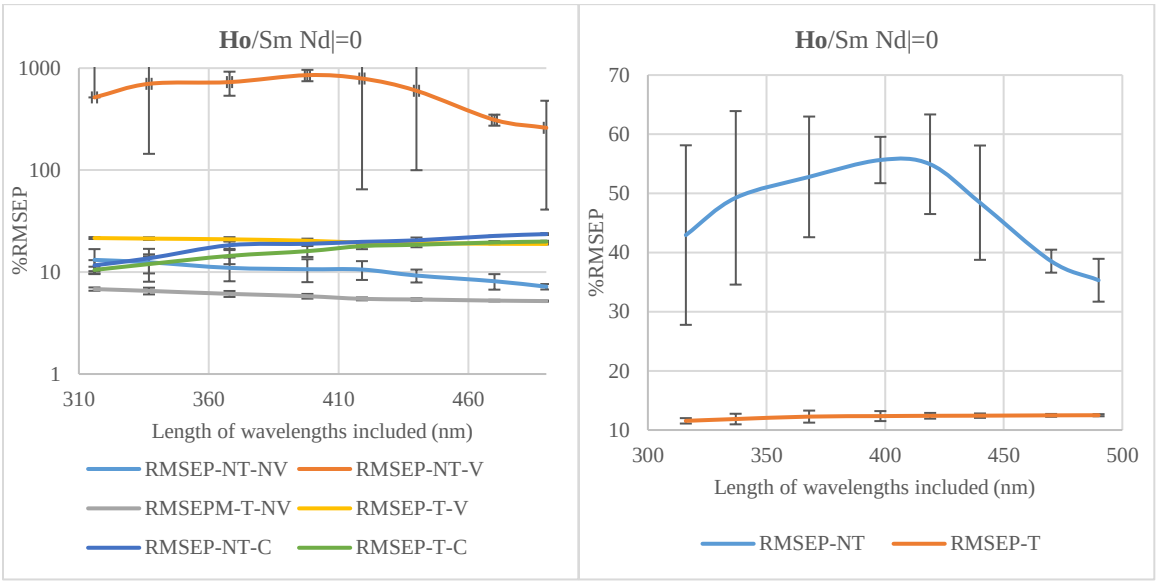


Figure 7.9. Samarium Models with Results. Including a Surrogate in the Training Set Improved Model Performance Against Contaminants Compared to None.



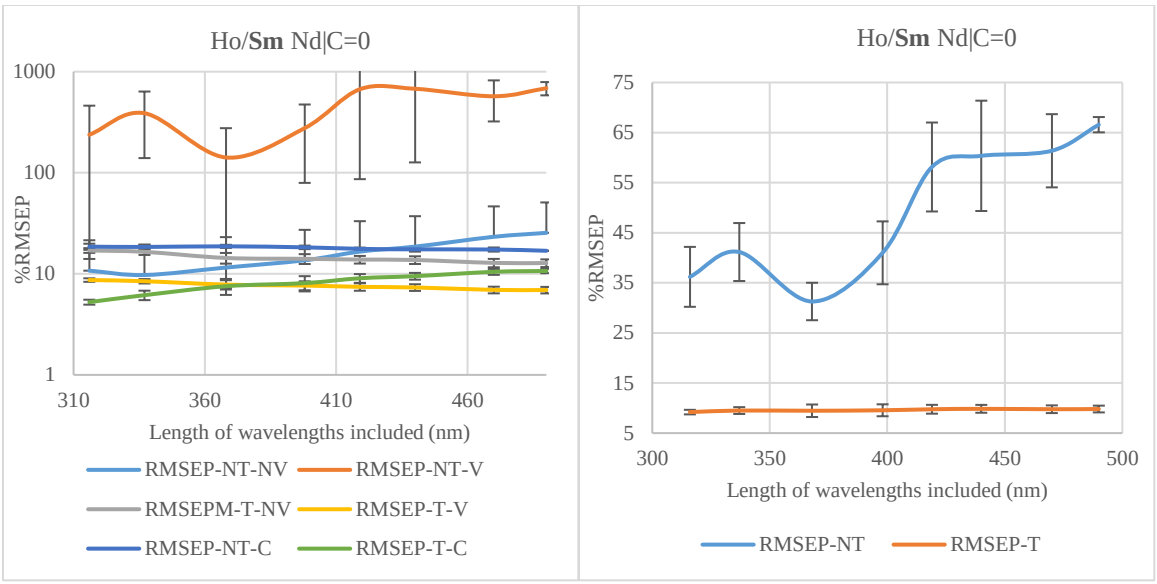
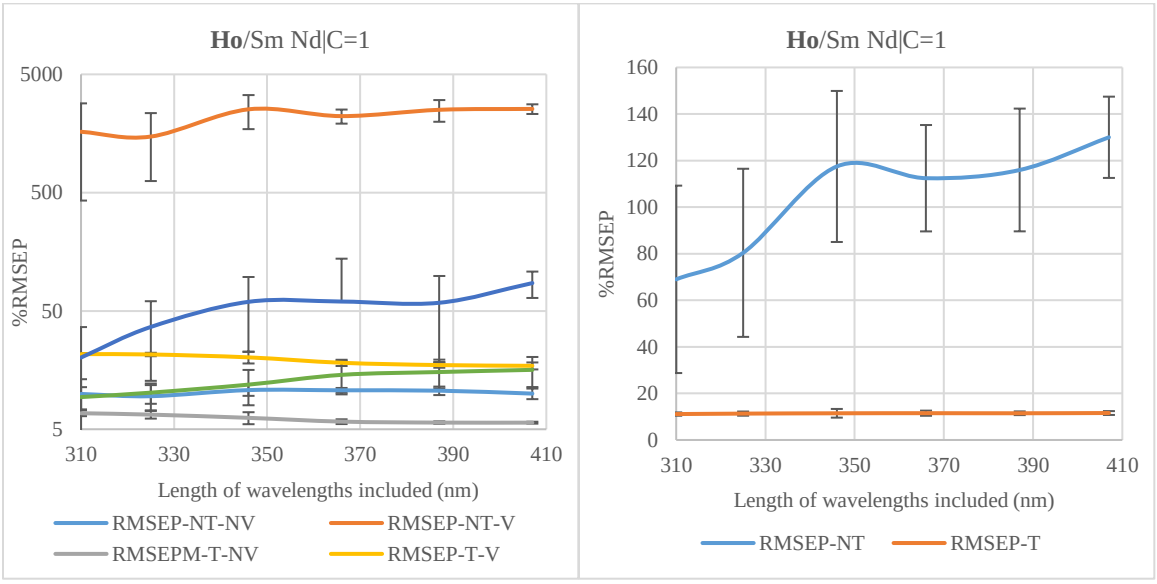


Figure 7.10. Models Utilizing Multiple Target Metals had Enhanced Performance due to Both Targets Acting as Surrogates for Each Other. Including Additional Surrogates Further Improves Results. The Top Graphs Shows Results for Holmium, While the Bottom is for Samarium.



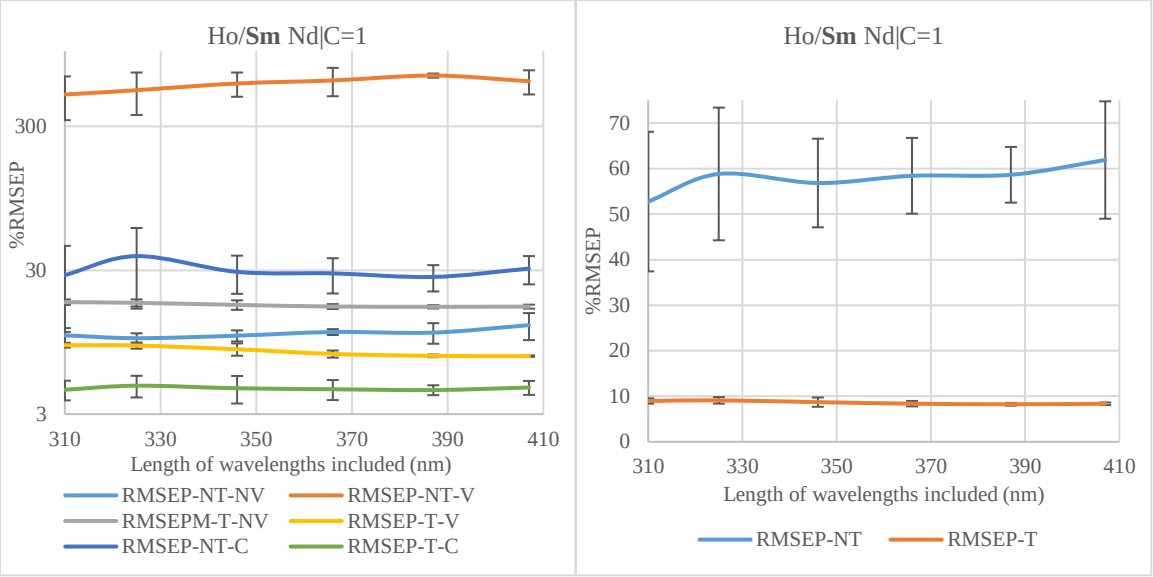


Figure 7.11. Models Utilizing Multiple Target Metals had Enhanced Performance Especially When All Additional Wavelengths Include Absorbance Peaks of Potential Contaminants. The Top Graphs Shows Results for Holmium, While the Bottom is for Samarium.

An additional set of trials using Samarium as a target metal was utilized, as shown in Figure 7.8, 7.9 and bottom set of Figures 7.10 and 7.11. Similar to the Holmium set, the worst-case scenario showed that model confusion could be increased in the contaminant set with increasing wavelength.

In the samarium set, the overall model performance decreased in both training sets with inclusion of additional wavelengths. The effect is more noticeable, likely due to the original set of absorbing wavelengths utilized to model Samarium were much smaller.

In the best case scenario for the Samarium set, the models where the surrogate was included showed model performance increase with additional wavelength inclusion. Further, as in most cases, the variance between model set errors is significantly lower, implying more reproducible results.

The averaging of the three test sets shows inclusion of contaminants in the training set does not lead to model confusion but rather prevents it, as there is a very slight decline in error with additional wavelengths.

Another set of models were generated using both Holmium and Samarium as target metals. The bolded Ho implies the figure is showing the output for the Holmium metal. The next set is the output for the Samarium metal, from the same model. The increase in error is less noticeable when including an additional model metal. This is likely due to the same effect of the surrogate playing into the target metal; the second target metal can act as a surrogate also and distinguish noise from signal.

Though the worst-case scenario (in which no additional wavelengths absorb where the contaminant does) decrease accuracy of the model, its decrease is small, and when coupled with the low probability of occurrence, does not outweigh the benefit of potentially choosing a correct wavelength of absorbing contaminant. Therefore, it is argued that including additional wavelengths is worthwhile. Further, utilizing the full spectrum is the suggested path for modeling, because it does not decrease accuracy enough to outweigh the gained benefit of safeguarding against model confusion.

7.3 Regression Vector

After interrogating the model performance improvement via additional wavelengths, we inspected the effect on the regression vector, as this would confirm the additional wavelengths

are utilized to differentiate between metals. Four samples are shown below from a set of models where Holmium and Samarium are target metals, and additional wavelengths added (facilitating the change from short to long window) are at locations where both contaminant and surrogate absorb, though the absorbance of the contaminant is inconsequential, as this is modeling data, not validation.

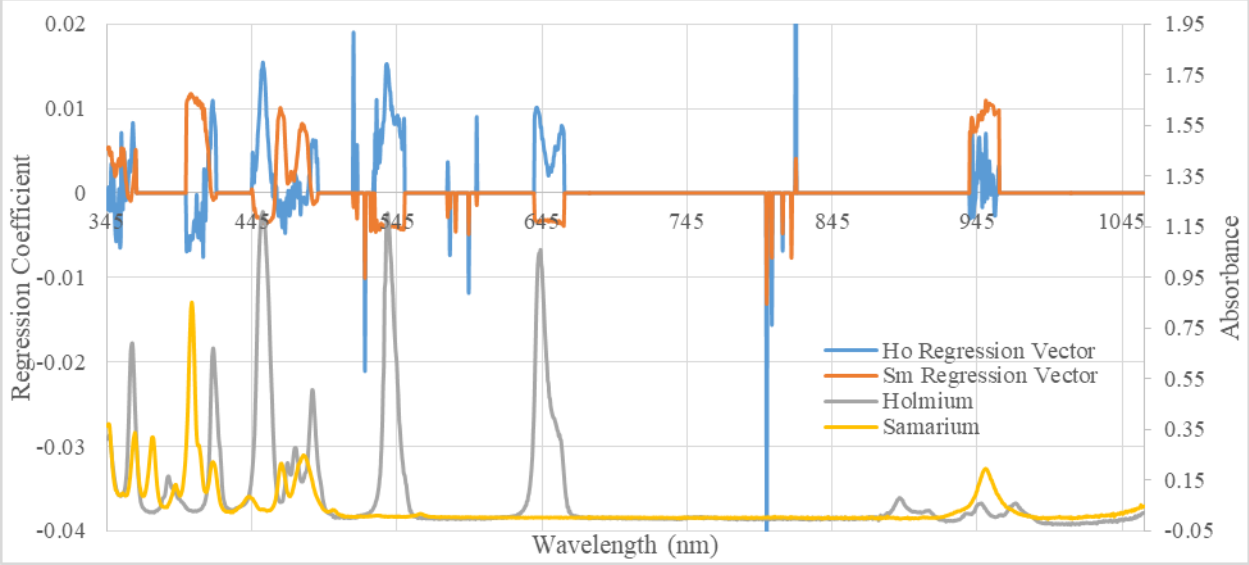


Figure 7.12. The Regression Vector Incorrectly Correlates Metal Concentration with Wavelengths with Non-Absorption.

The above graph shows the regression coefficients overlaid the absorbance spectra of the metals. In both the Samarium and Holmium regression vectors, there are wavelengths with very high coefficients (515 nm, 520 nm, 800 nm, and 820 nm) that do not correspond to absorbance of any present metal. This is the model correlating noise, and thus decreasing accuracy. In the case of Holmium, a metal absorbing from 820 onwards (and not at 800) will largely skew the predicted concentration.

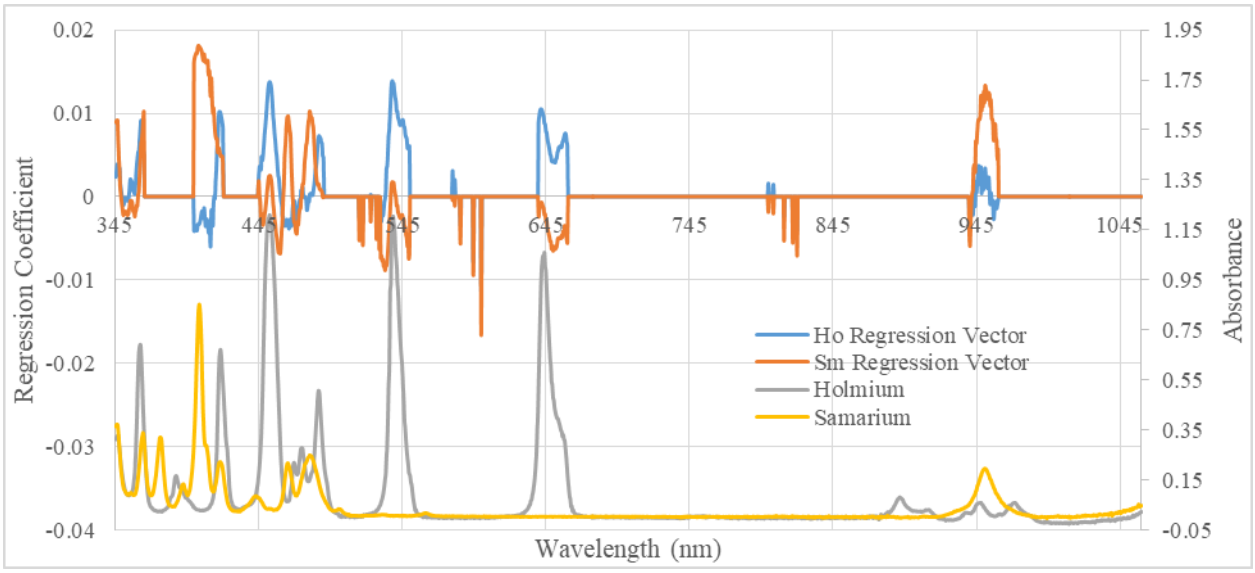


Figure 7.13. Inclusion of Surrogate Reduces Correlation between Target Metal and Non-Absorbing Species. Further, the Correlation that Does Exist is Negative.

Inclusion of the Neodymium surrogate reduced regression coefficients at non-absorbing wavelengths for Holmium and Samarium, and in most cases it became negative. This is due to the model being able to correlate absorbance not congruent with changes in metal concentration appear there. Thus, a contaminant absorbing there will reduce the calculation of concentration for the target metal. This is desirable because if a contaminant also absorbs at a band alongside targets Holmium or Samarium (causing an artificial inflation of prediction), the model will then reduce that calculation.

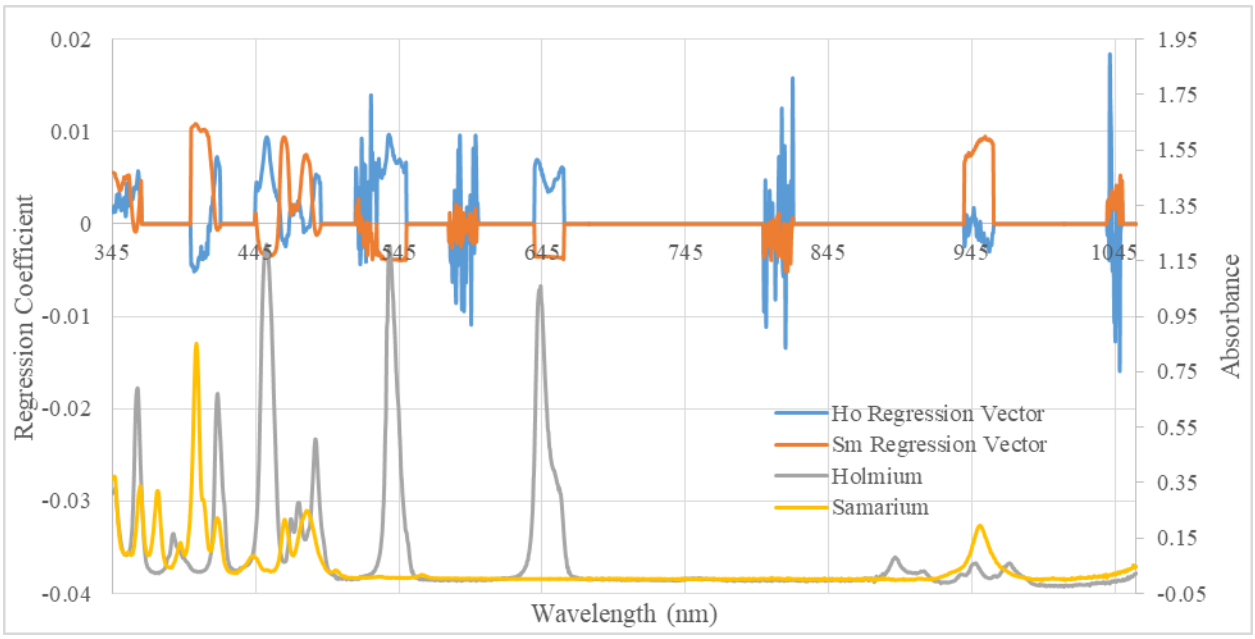


Figure 7.14. Including Additional Wavelengths Decreases Correlation between Target Metal and Non-Absorbing Wavelengths, Providing Additional Discrimination.

Expanding the window (number of wavelengths examined) has a positive though less pronounced effect.

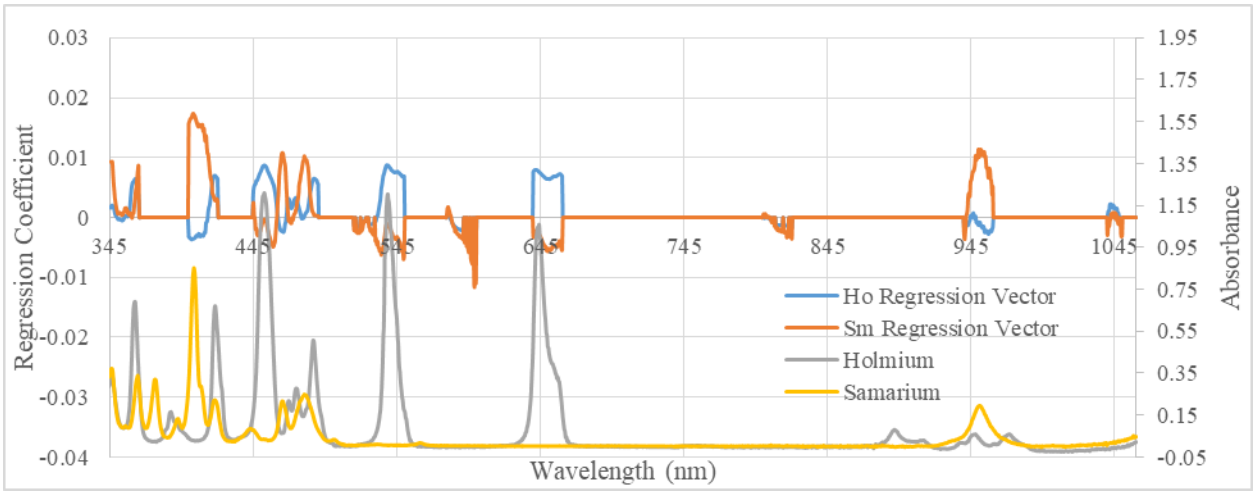


Figure 7.15. Including Additional Wavelengths and a Surrogate Contaminant Minimizes Correlation between Target and Non-Absorbing Wavelengths. Further, Correlation is Exclusively Negative.

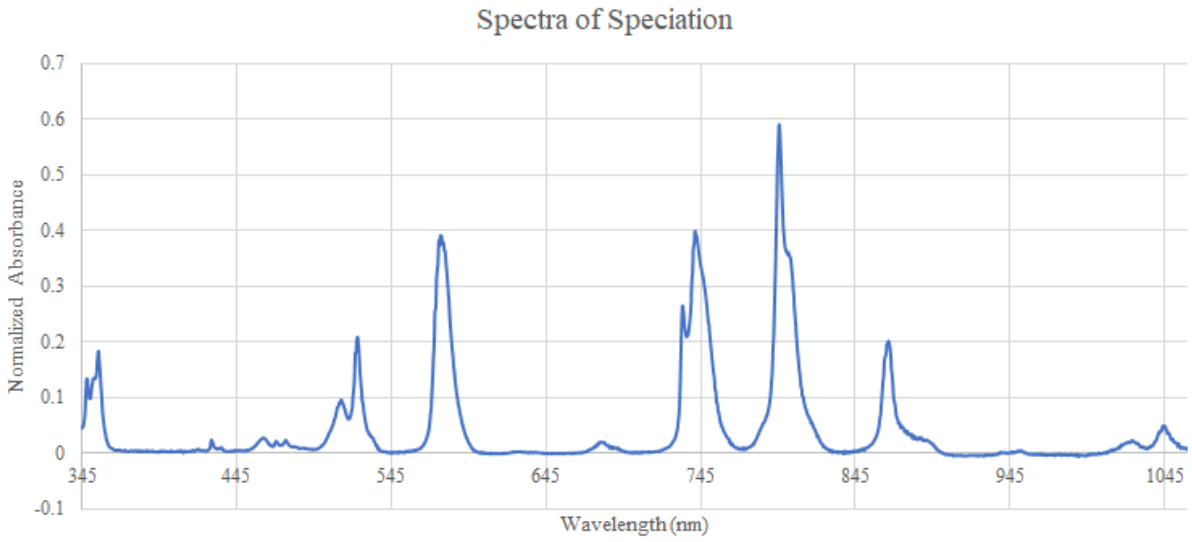
The research here supports the hypothesis that expanding the window of wavelengths examined for a model can improve model accuracy when more than one species is present, whether that means contaminates or multiple metal targets. For the purpose of safeguarding, it is preferential to include more wavelengths because it allows for greater metal discrimination and thus more robust tracking and safeguarding.

CHAPTER 8: Speciation Modeling of Neodymium and Citrate

The last set of experiments for this thesis were to track the speciation of Nd with Citrate at varying pH's via UV/Vis. Literature already shows the concentrations for these species can be calculated from starting conditions and pH.

8.1 Speciation Observance via UV/Vis

The preliminary research into the speciation of Nd with Cit was to probe how large of an effect was observable. This was done by creating varying mixtures of Nd, Cit, and KOH. Absorbance was recorded as KOH was added to a mixture of concentrated Nd and Cit. The following graphs illustrate the most extreme cases; starting 1 M Nd, 1 M Citrate, and no KOH added to give a solution of pH ~1 for the first, then starting 1 M Nd, 1 M Citrate, and KOH added to give a solution pH of ~5. Note, the addition of the KOH diluted the Nd and citrate, but not significantly, and the absorbance is normalized to the same Nd and Cit concentrations.



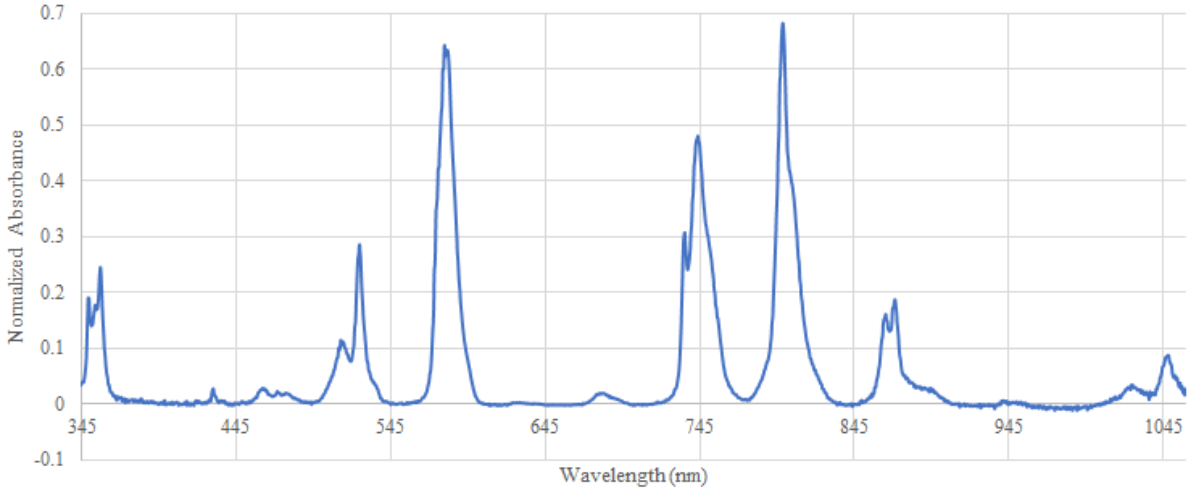


Figure 8.1. Comparison of Spectra with Pure Neodymium (Top) and Complexation with Citrate (Bottom).

The differences between spectra are subtle but present. Foremost, peaks at 350, 525, 560, 745, 790, became more absorptive. This implies more light is being absorbed by this electron, which would be caused by a larger difference between LUMO and HOMO. Though difficult to see here, many of the peaks redshift, implying the electrons are more easily excitable due to longer wavelengths (less energy light) causing absorption. Finally, the most noticeable feature, is the splitting of the peak at 870 nm. Though it is not known, a potential explanation could be the light at that wavelength would excite the electron into a state occupied by a binding electron provided by the citrate. Figure 8.4 also depicts this shift across multiple spectra from pH 1 to 7. Figure 8.9 shows the most detailed changes, as only select peaks are showcased, and features such as the splitting of the 800 nm peak are more observable.

Figure 8.2. Neodymium complexes with hydroxides at pH 3 or higher when there is less than twice the concentration of Citrate as Neodymium.

When generating samples of Neodymium, Citrate, and Potassium Hydroxide, one unanticipated phenomenon occurred. Neodymium crashed out of solution at relatively low pH's (higher than 3) when the ratio of Neodymium to Citrate was not substantial (at least 1:2 Nd to Citrate) as shown in Figure 8.2. Due to this causing the solution to turn turbid (and over the course of a day the molecules would precipitate), this made UV/Vis absorption impossible, as the Beer-Lambert law is no longer valid. After creating ten dozen sample sets, varying concentration of three components, it was clear that having more citrate than neodymium allowed for richer pH profiles without the metal precipitating. The graph below illustrates that samples could not be made with pH above 4 unless there was twice the citrate as neodymium. Once the ratio was 3, it allowed for a full pH profile up to pH 14. This data was gathered but not used, as it did not become relevant to observe species present over pH 7.

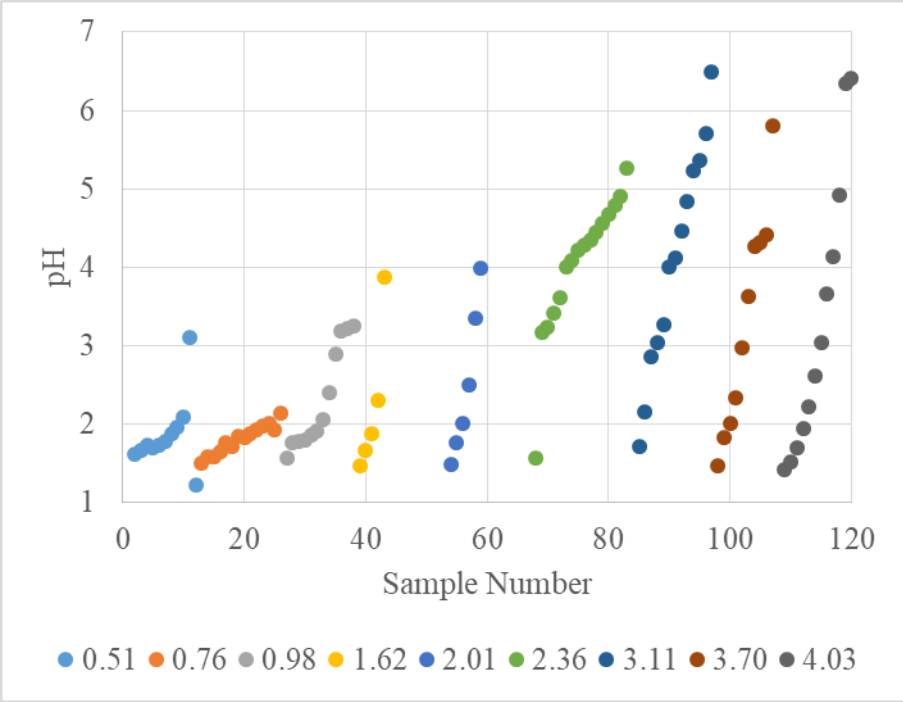


Figure 8.3. Samples Made at Varying Neodymium to Citrate Ratio. With More Nd than Cit, Larger pH Profiles Were Possible.

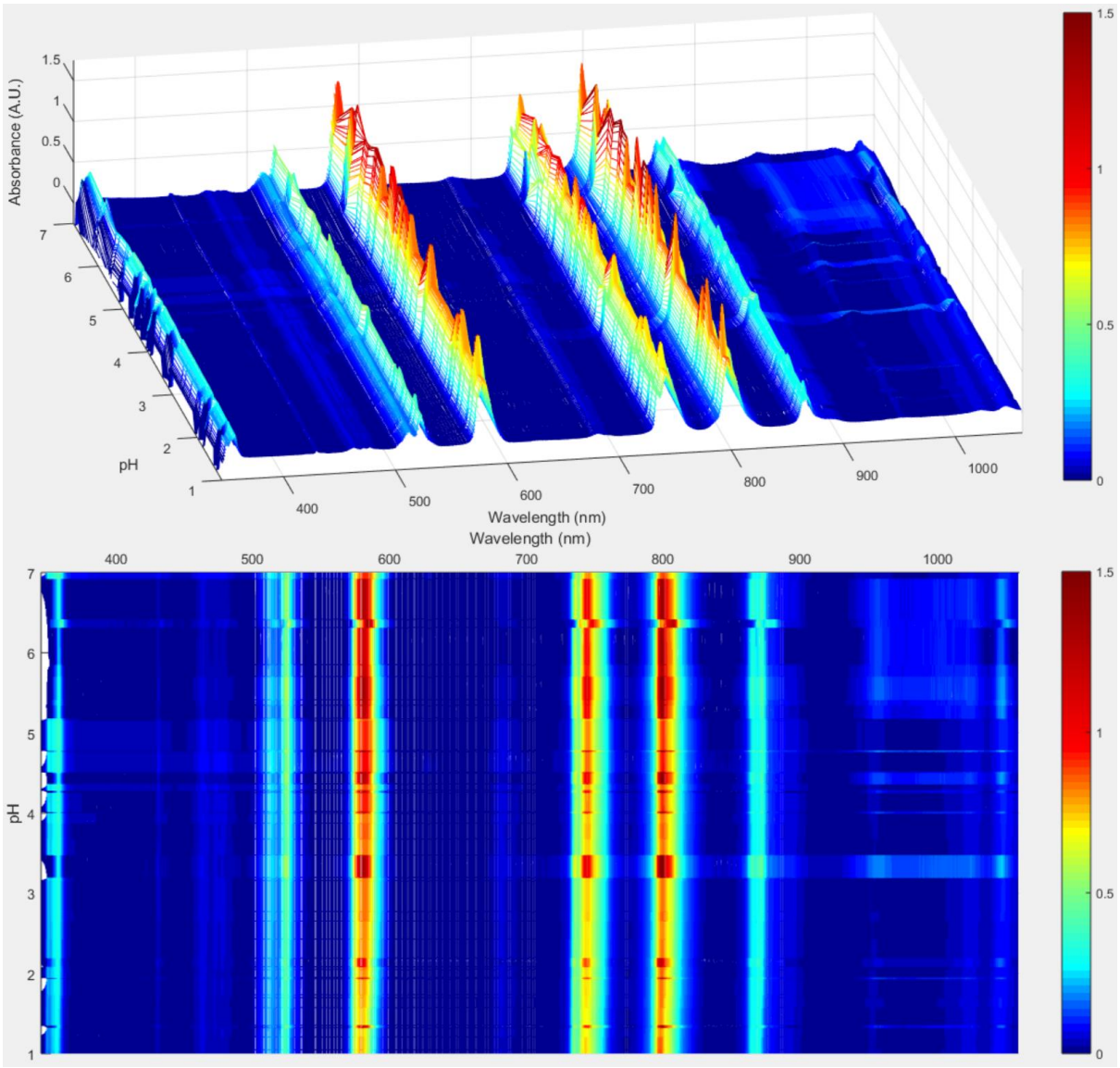


Figure 8.4. Aggregate of Multiple Spectra from pH 1 to 7. Absorbance Increases and Redshifts for Most Peaks.

A second set of experiments were ran using varying concentrations of constant volume additions of KOH. Due to results showing a higher Citrate than Neodymium concentration was desirable, all samples were at a ratio of roughly 3:1 ligand to metal. This changed the equilibrium slightly which is shown in the following section.

8.2 Correlation of Speciation Change and Spectral Shifts

Though the speciation changes were observable, this did not immediately make them modelable. To do so required precise knowledge of the species concentrations. As stated previously, research by other groups had already determined the stability constants of the complexes present in the neodymium-citrate system[119]. Those values are listed in equations (1):(7). The neodymium species logarithmic stability constants are 6.94 for NdCit, 9.5 for NdHCit, 10.91 for $NdCit_2$, and 14.5 for $NdHCit_2$. The three sole citrate species are 12.12 for H_3Cit, 9.33 for H_2Cit, and 5.23 for HCit.

$$\frac{[NdCit]}{[Nd][Cit]} = 10^{6.94} \text{ (1)} \quad \frac{[NdHCit]}{[Nd][H][Cit]} = 10^{9.5} \text{ (2)} \frac{[NdCit_2]}{[Nd][Cit]^2} = 10^{10.91} \text{ (3)} \frac{[NdHCit_2]}{[Nd][H][Cit]^2} = 10^{14.5} \text{ (4)}$$

$$\frac{[H_3Cit]}{[H]^3[Cit]} = 10^{12.12} \text{ (5)} \quad \frac{[H_2Cit]}{[H]^2[Cit]} = 10^{9.33} \text{ (6)} \quad \frac{[HCit]}{[H][Cit]} = 10^{5.23} \text{ (7)}$$

Using these seven equations and constants, the two equations (8) and (9) representing a total neodymium and a citrate balance. Note, the subscript of 't' denotes the total of the material. This is a known quantity because the starting quantity was measured. What is unknown is the sole species concentration of [Nd] and $[H_3Cit]$, representing the uncomplexed molecules.

$$[Nd]_t = 10^{-5.18} \cdot \frac{[Nd][H_3Cit]}{[H]^3} + 10^{-2.62} \cdot \frac{[Nd][H_3Cit]}{[H]^2} + 10^{-13.33} \cdot \frac{[Nd][H_3Cit]^2}{[H]^6} + 10^{-9.74} \cdot \frac{[Nd][H_3Cit]^2}{[H]^5} + [Nd] \quad (8)$$

$$[Cit]_t = [H_3Cit] + 10^{-2.79} \cdot \frac{[H_3Cit]}{[H]} + 10^{-6.89} \cdot \frac{[H_3Cit]}{[H]^2} + 10^{-12.12} \cdot \frac{[H_3Cit]}{[H]^3} + 10^{-5.18} \cdot \frac{[Nd][H_3Cit]}{[H]^3} +$$

$$[Nd] \cdot \frac{[H_3Cit]}{[H]^2} \cdot 10^{-2.62} + 2 \cdot [Nd] \cdot \frac{[H_3Cit]^2}{[H]^5} \cdot 10^{-9.74} + 2 \cdot [Nd] \cdot \frac{[H_3Cit]^2}{[H]^6} \cdot 10^{-13.33} \quad (9)$$

Equation 8 was rearranged to solve for the sole neodymium concentration in equation 10, and equation 9 was rearranged to find the undissociated citric acid concentration in equation 11.

$$[Nd] = {[Nd]_t} \Big/ \left(10^{-5.18} \cdot \frac{[H_3Cit]}{[H]^3} + 10^{-2.62} \cdot \frac{[H_3Cit]}{[H]^2} + 10^{-13.33} \cdot \frac{[H_3Cit]^2}{[H]^6} + 10^{-9.24} \cdot \frac{[H_3Cit]^2}{[H]^5} + 1\right) \quad (10)$$

$$[H_3Cit] = \frac{\left\{\sqrt{\left(\frac{10^{-2.79}}{[H]}+\frac{10^{-6.89}}{[H]^2}+\frac{10^{-12.12}}{[H]^3}+\frac{10^{-5.18}\cdot[Nd]}{[H]^3}+\frac{10^{-2.62}\cdot[Nd]}{[H]^2}+1\right)^2 + 4\cdot[Cit]_t\cdot\left(2\cdot\frac{10^{-13.33}\cdot[Nd]}{[H]^6}+2\cdot\frac{10^{-9.74}\cdot[Nd]}{[H]^5}\right)} - \frac{10^{-2.79}}{[H]} - \frac{10^{-6.89}}{[H]^2} - \frac{10^{-12.12}}{[H]^3} - \frac{10^{-5.18}\cdot[Nd]}{[H]^3} - \frac{10^{-2.62}\cdot[Nd]}{[H]^2} - 1\right\}}{\left\{4\cdot[Nd]\cdot\left(\frac{10^{-13.33}}{[H]^6}+\frac{10^{-9.74}}{[H]^5}\right)\right\}} \quad (11)$$

The end result was two equations (eq. 10 and 11) and two unknowns ([Nd] and [H_3Cit]). These two equations were coupled which means they could not be solved directly. The equations were solved iteratively, by guessing an initial value of [Nd] and calculating a value of [H_3Cit] via eq. 11, then using that value in eq. 10 to calculate [Nd] and so on until the values stopped changing between iterations. Initial guesses were made between 0 [Nd], and the initial starting concentration of [Nd], representing 0 to 100% free [Nd]. Initial guesses did not have an influence on the final value. The results are plotted below.

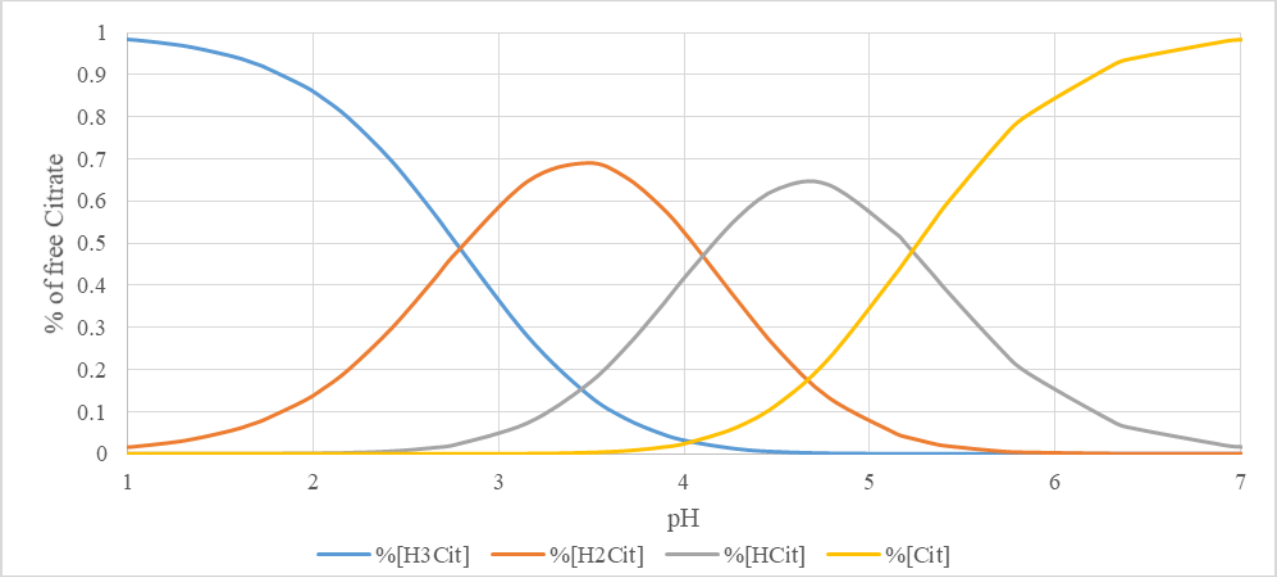


Figure 8.5. Speciation Diagram for Four Citrate Complexes of Varying Protonation. Species are shown in percent of total citrate.

The above graph is the speciation diagram of Citrate complexes. Note that the values are in percent of free citrate, meaning the citrate complexed with neodymium is not included. This is due to increasing pH creates more citrate bound to Nd than free in solution, which makes the data difficult to read, as the lower pH values are inherently higher in concentration.

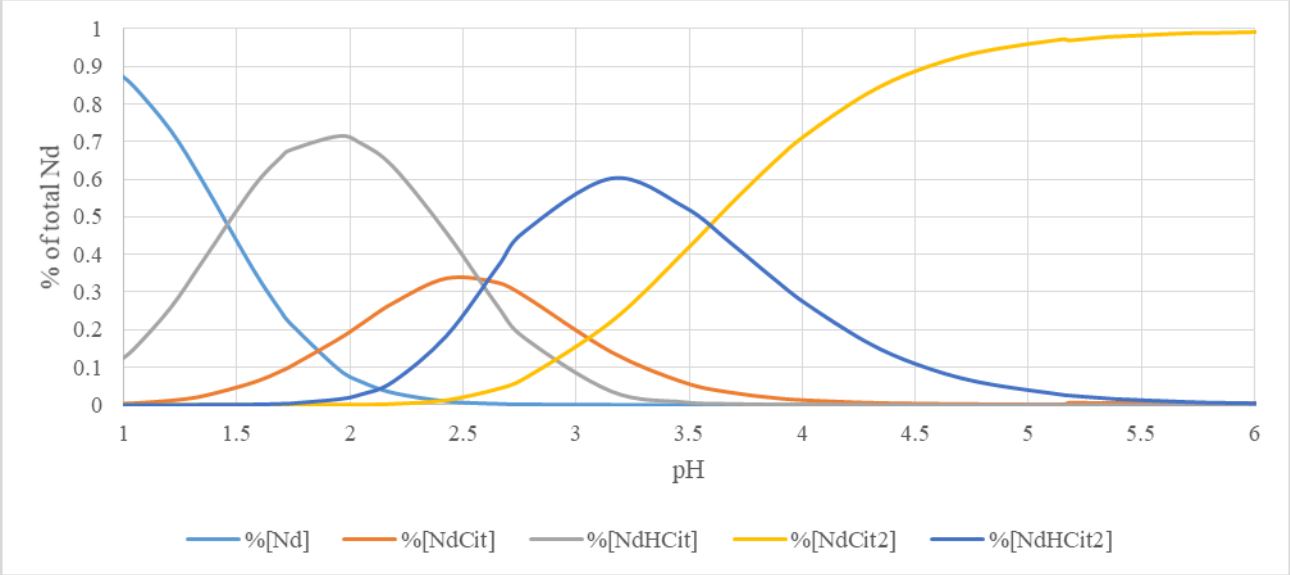


Figure 8.6. Speciation Diagram for Five Neodymium and Citrate Complexes Across pH Profile. Results Are Specifically of 3.2:1 Citrate to Neodymium Ratio.

The above graph is the speciation diagram of Neodymium complexes. Like the citrate, the values are in percent of neodymium, where 100% represents the total starting concentration of neodymium.

After creating solutions of metal and ligand, the UV/Vis absorbance of samples were recorded. The results are shown below in contour plots. The first graphic is an overview of the data, while the second is more informative. The general trend is peaks undergo both bathochromic and hyperchromic shifts. Peaks at 590, 760, and 800 nm increase in absorbance at higher pH, while most peaks broaden while also shifting, to give their higher wavelength edge an around 5 nm shift across the pH spectrum.

After recording the absorbance shift across the entire pH spectrum, we believed that the amount of variance between spectra was low, and especially considering it would be used to differentiate between five different species. As the protonation of a complex would not cause a drastic absorbance shift, we believed it would be easier to model the system using combined protonated and non-protonated species, which shifts the speciation curve as seen below.

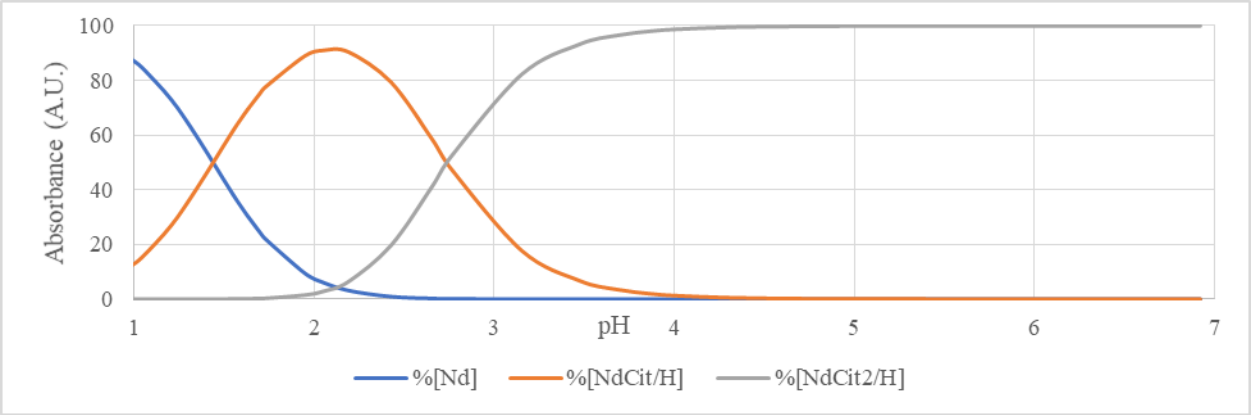


Figure 8.7. Combining Protonated and Non-Protonated Species Allows for More Distinct Species. Results Are Specifically of 3.2:1 Citrate to Neodymium Ratio.

This change is further supported when examining spectra at specific pH. The below comparison is samples taken at pH of a maximum of each species relative concentration. In the

combined species, there is noticeable differentiation between the three species, though the NdCit/H is more of an intermediate and does not have unique features not found in either pure Nd spectrum or the $NdCit_2$/H spectrum. However, this is still preferred to the individual complexes spectrum, where each species does not contribute noticeably enough to change the spectra; specifically NdCit and NdHCit are hardly distinguishable, and is $NdCit_2$ when compared to $NdHCit_2$, which has nearly perfect overlap.

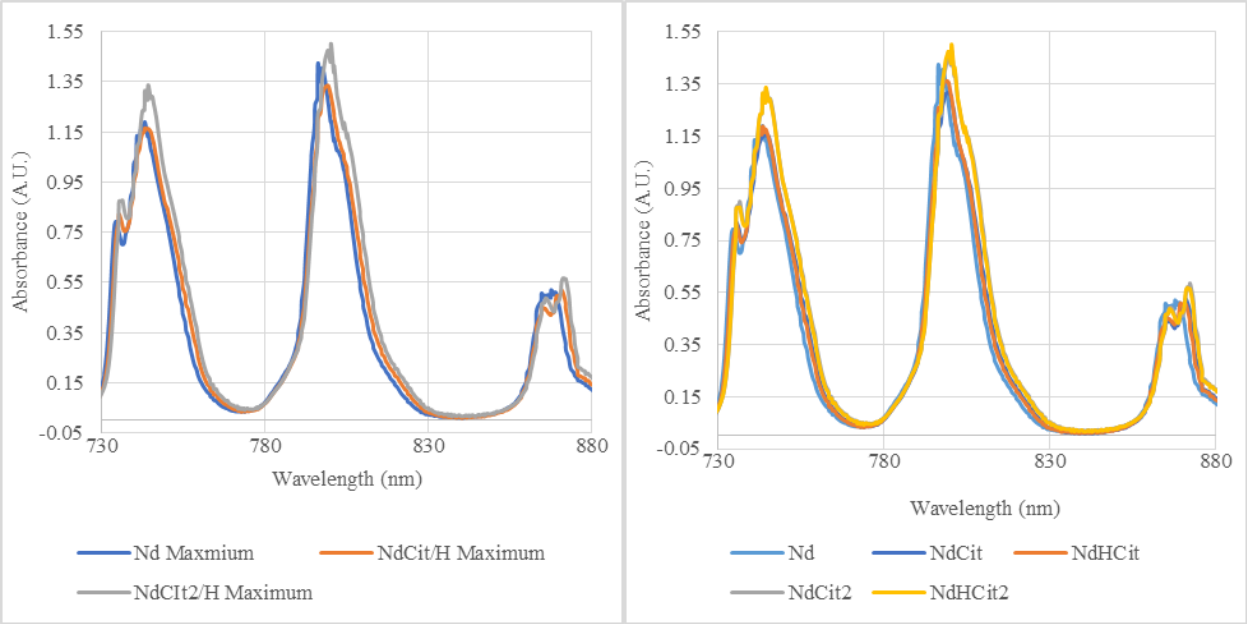


Figure 8.8. Comparison of Spectra from Samples at pH with given Complexations are at Maximum.

8.3 Modeling Results

More detailed graphs are shown below of individual peaks. In all four graphs, it can be seen the lower end pH (1-2) has a right edge around 5 nm less than at higher pH. Also, the intensity of the absorbance increases quickly with increasing pH. In the bottom left graph, showing peaks at around 865 nm, it can be seen at low pH, there is a single peak, however this peak splits into two peaks after around pH 3. These are indicative of speciation.

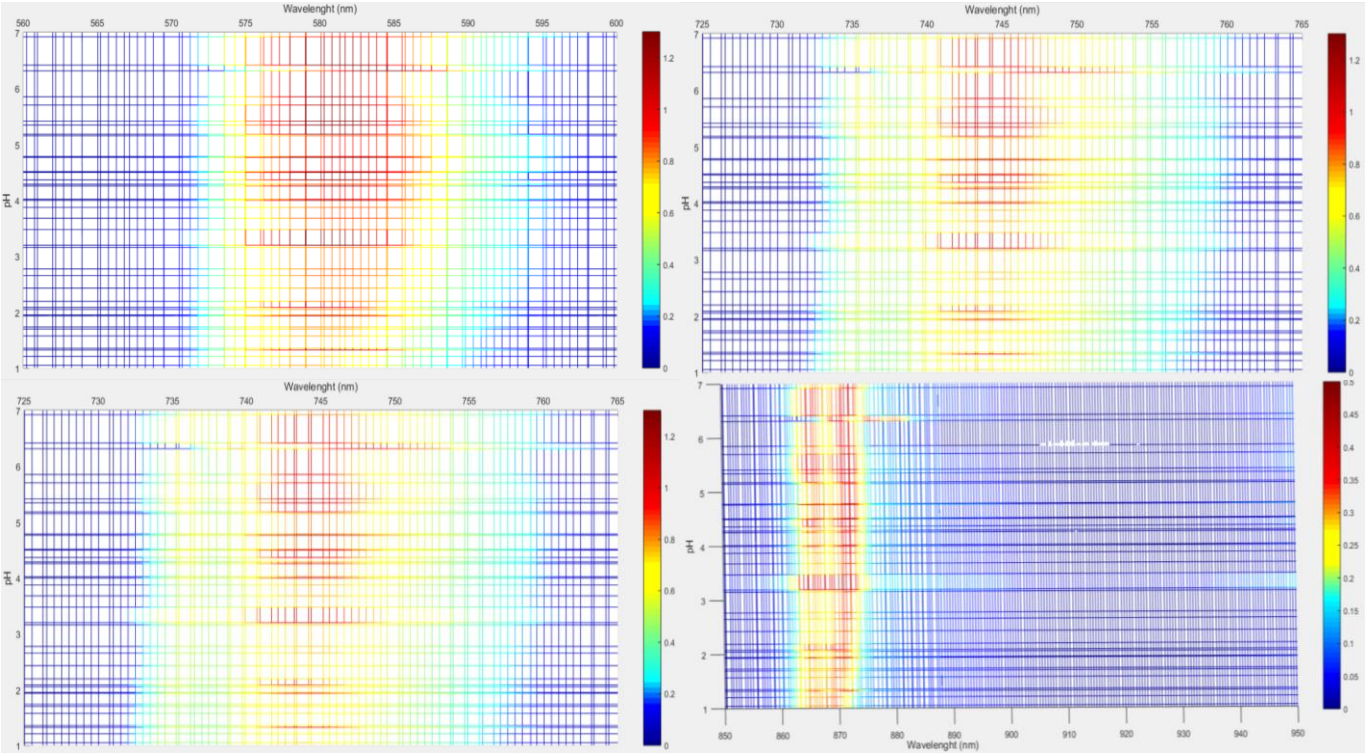


Figure 8.9. Examination of Peaks at Given pH. Absorbance Generally Increases and Red Shifts. Peak at 800 nm Splits.

The data was input to the PLS modeling software, and a model was created utilizing 7 LV's. The outputs are shown below. The %RMSECV is on average 23% for the metal complexes. The average CV predicted pH was 8% off the measured value. From examining the spectra shifts, the majority of the changes occurs between pH 1 to 4. This explains why CV predicted pH is more accurate between pH 1 to 4 (average 6%) than pH 4 to 7 (average 12%).

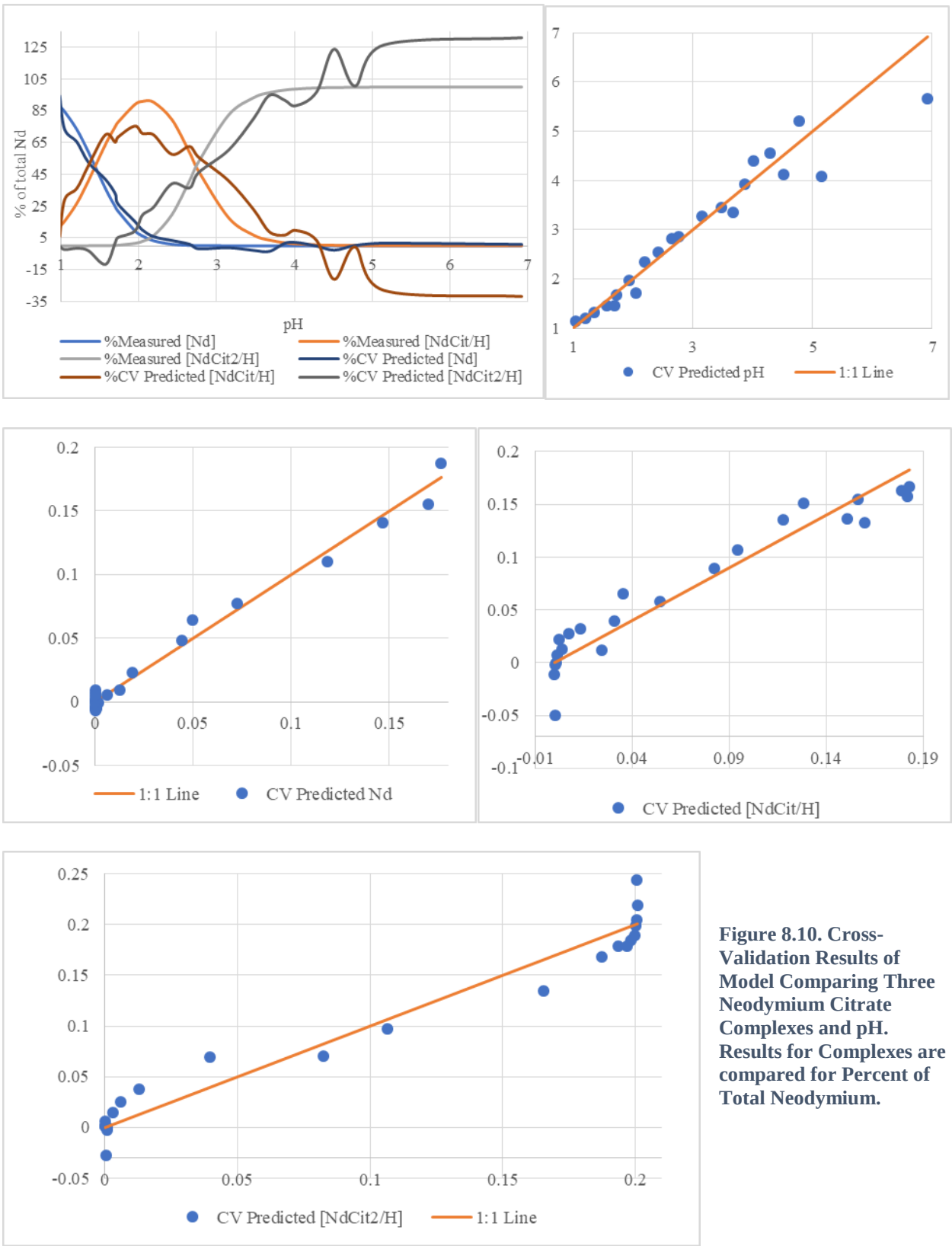


Figure 8.10. Cross-Validation Results of Model Comparing Three Neodymium Citrate Complexes and pH. Results for Complexes are compared for Percent of Total Neodymium.

With the speciation changes being more observable at lower pH, this manifests in the larger complexes (NdCit and to a more extent $NdCit_2$ along with their protonated species) being more difficult to model, while pure Nd is the easiest modeled.

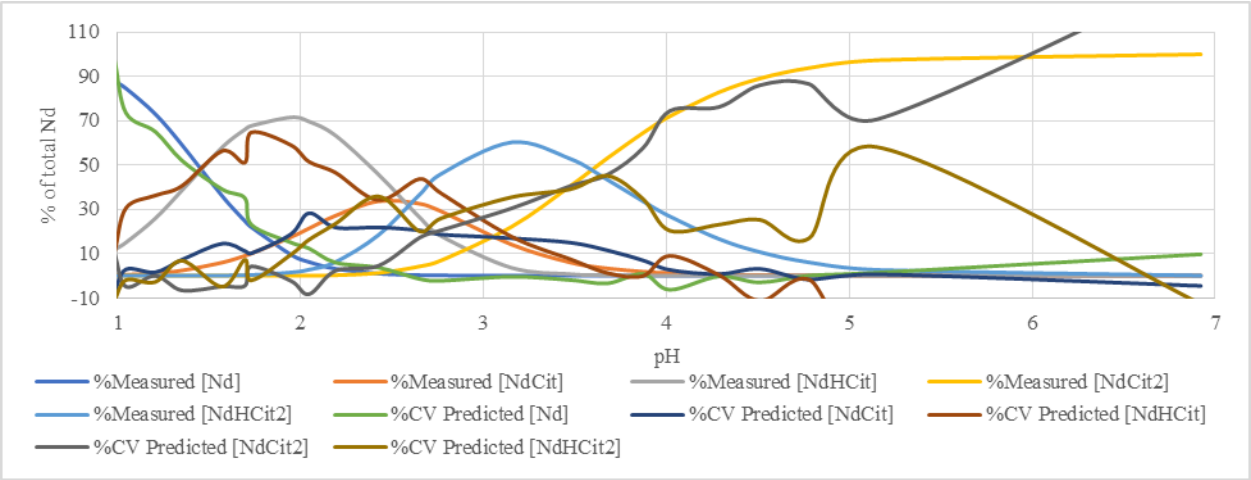


Figure 8.11. Cross-Validation Results of Model Comparing Five Neodymium Citrate Complexes. Results are compared for Percent of Total Neodymium. Five Species Creates Much Worse Results.

Data was modeled with both combined species (defining NdHCit and NdCit as one, along with $NdCit_2$ and $NdHCit_2$), and separate species. Though originally we suspected the individual species would create very poor models, we needed to confirm it still. Direct comparisons of this is shown above in Figure 8.11. Overall, the model performance increased drastically when combined species were implemented rather than individual species, as the average %RMSECV of the metal complexes were 42% (decreased by 20% when combining species). The one benefit is the model tracks species from pH 1 to 5, as the less complex version stops seeing speciation changes after pH 4, therefore the more complex version, though less accurate, monitors changes over a wider pH window.

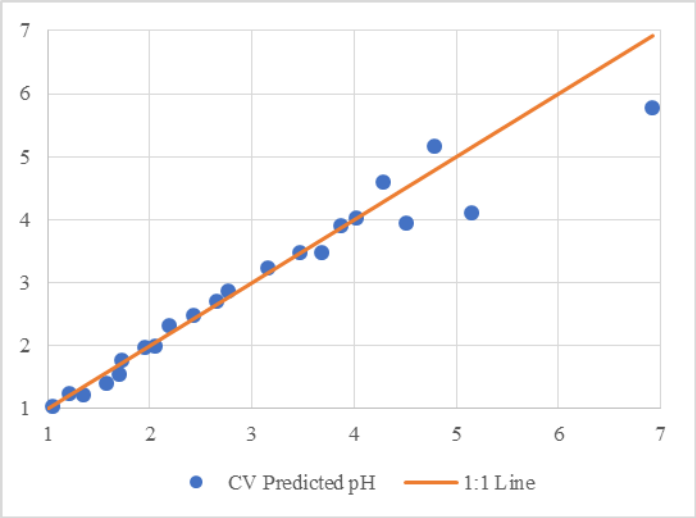


Figure 8.12. Cross-Validation Results for Prediction of pH based on Absorbance. Performance is Improved Marginally compared to Three Species Result.

After taking the model to higher complexity, we also reduced complexity to observe performance changes. All complexed species were combined as one variable, pH and uncomplexed Neodymium were left alone. The results of the RMSECV are shown below in Table 8.1 and Figure 8.13. The overall model accuracy increased from 20% to 16% though there was a decrease in complexity as all complexed species are lumped into one form. From a safeguard standpoint this could be undesirable as changes in pH at higher values (where the model already underperforms) would go undetected from a speciation standpoint as the sum of the double and single citrated species would not change.

Variable	Neodymium	Complexed Nd	pH	Overall
RMSECV	0.012	0.012	0.450	
%RMSECV	34.28%	7.38%	15.35%	15.72%

Table 8.1. RMSECV Results for Model of pH and Neodymium in Pure and Complexed Form.

Variable	Neodymium	NdCit/H	$NdCit_2/H$	pH	Overall
RMSECV	0.011	0.011	0.022	0.350	
%RMSECV	31.93%	16.26%	23.16%	11.92%	19.46%

Table 8.2. RMSECV Results for Model of pH, Neodymium and Complexed Citrate Species.

Variable	Neodymium	NdCit	NdHCit	$NdCit_2$	$NdHCit_2$	pH	Overall
RMSECV	0.011	0.012	0.028	0.023	0.033	0.368	
%RMSECV	31.17%	63.93%	54.73%	36.22%	103.79%	12.56%	41.56%

Table 8.3. RMSECV Results for Model of pH, Neodymium and Individual Citrate Species.

The research here supports that the speciation of metal ions can be observed and modeled via UV/Vis absorption. Though the conecentrations of species were less accurate than the model would need be for materials safeguarding, it shows there is potential for doing so. Further, the pH can be tracked relatively well that can be indicative of process changes. This is an attractive potential for this system as this creates another physical process unique to current safeguard methods that would require falsification in order for an inside actor to divert material.

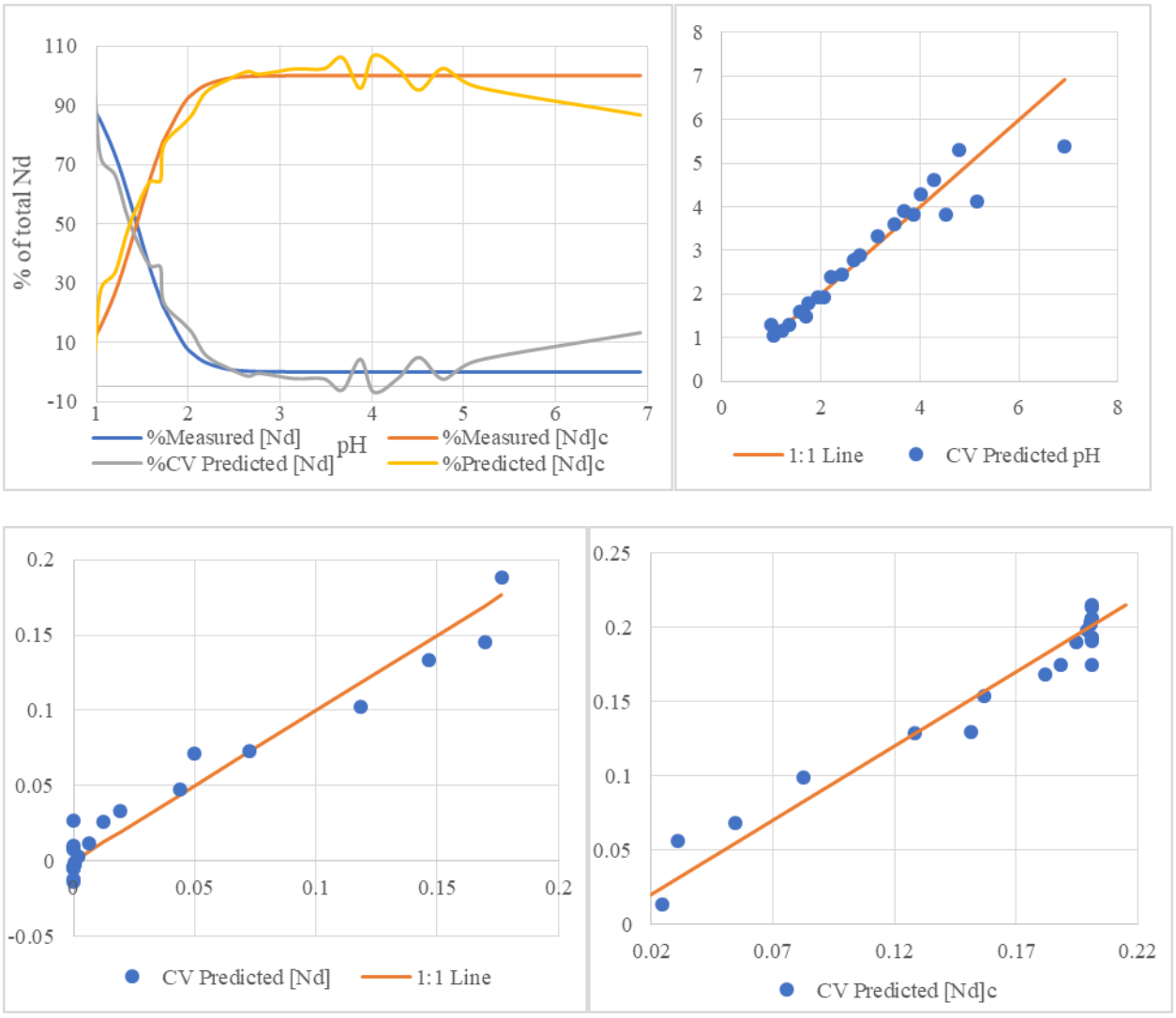


Figure 8.13. Cross-Validation Results of Model Comparing Two Neodymium Based Species. Results are compared for Percent of Total Neodymium. Two Species Creates Better Results at the Cost of Complexity.

Chapter 9: Conclusion

The objective of the thesis was to understand how used nuclear fuel recycling can be better implemented to mitigate the intensity of the destruction climate change will bring. By heavily decarbonizing our electric grid via nuclear energy, climate change goals become both realistic and affordable. However, an increase in nuclear energy prevalence necessarily increases the threat of nuclear proliferation[126]. Thus, the thesis sought how to mitigate this problem, so the threat to life and wellbeing is reduced, and not just challenged in a different way. Research sought to understand and suggest solutions to both political and scientific challenges of nuclear fuel recycling. The process of nuclear fuel recycling will inherently threaten life. However, the severity and probability of this threat can be minimized to where its benefit vastly outweighs its cost.

As nuclear energy spreads across the globe, it will undoubtedly cross borders into less safe territories. Denying long-term clean energy will have severe ramifications, and thus minimizing the nuclear process in this region directly minimizes the danger. International fuel banks, recycling centers, and enrichment plants can all contribute to taking large key elements of nuclear threat out of less secure countries. This also grows international cooperation and introduces a new level of scrutiny as it removes one country's complete oversight of the process. This method of mitigating nuclear threat can help countries such as Saudi Arabia meet their energy needs while denying them the back routes to weapons development.

Parallel to suggesting a safer fuel recycling process on the international level, the thesis also sought to explore safety improvements on an industrial level. The tracking of special nuclear material in close to real time does not completely guarantee the safety of the process but resolves

a major security threat via inside actors. Utilizing UV/Vis spectra absorption to track both uranium and plutonium can monitor specific metals in close to real-time, while also being noninvasive and inexpensive.

The research sought to provide insight into the practicality and ease of multi-component modeling. As there exists an array of advanced fuel recycling techniques, and the complexity increases when each reactor will have a unique spent fuel make up, it is impossible to provide one catch-all model for tracking material. By studying how to successfully model materials in solution, it would allow for high reproducibility of the models made in this research. Rather, being able to make models easily was seen as more practical. Additionally, as fuel recycling is seen as an inherent threat to life and safety, the research focused on minimizing security risks. Specifically, the research covered expanding spectra windows examined to create robustness against an inside actor from diverting material. Finally, as material in nuclear fuel recycling undergoes a multitude of chemical processes at varying conditions, it was of interest to study the spectra shifts due to speciation. Tracking the speciation via the UV/Vis absorbance would create an additional hurdle for a nefarious actor to cross in order to divert material.

The research of this thesis sought to provide information to how nuclear fuel recycling can be done in a more safe way to minimize proliferation threat. Nuclear proliferation is a problem society will have to live with and will take a momentous work to overcome, but climate change is not a problem society can live with. The consequences of our damage to the environment are too grave for society, and great action must be taken to reverse it. It is for this reason that nuclear energy is our best path going forward. It can reduce emissions far beyond what other technologies are capable of, and doing so safely must be our priority as a society to survive.

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